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INDUSTRIAL CHEMISTRY

A MANUAL FOR THE STUDENT AND MANUFACTURER

EDITED BY

ALLEN ROGERS

In charge of Industrial Chemistry, Pratt Institute, Brooklyn, N. Y.
Major, Chief Industrial Relations Branch, United States Army

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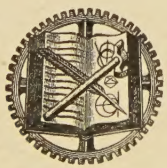

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PREFACE TO THIRD EDITION

While yet contemplating the appearance of a third edition of the Manual of Industrial Chemistry, we became aware that the fabric of American Industry was rapidly shaping itself under the influence of war into a marvelous structure, the importance of which was not only apparent to the industrial chemist but to the public at large.

We have thus been forced to enter a new era in our commercial development where the role to be played by the American chemist will be far-reaching in its effect upon our future prosperity. In order, therefore, that the chemists of the country may be somewhat assisted, by having the proper tools at their disposal, it has been deemed advisable to again bring this volume up-to-date, and thus, in a humble way, add to the efficiency and achievements of our profession.

The numerous collaborators have nobly responded to the call, even neglecting other important duties, in order that they might incorporate into their contributions the most modern methods and processes.

Some of the material appearing in the second edition has been eliminated, but to offset this four entirely new chapters have been introduced. Nearly every chapter has been revised and substantially enlarged. By this revision, over two hundred pages have been added to the text and over seventy new illustrations provided.

Many valuable suggestions have been received from those using the book, and an attempt has been made to incorporate them in the present volume. Constructive criticism is always welcome and it is hoped that the reader will feel that it is his book and will bear in mind that further suggestions for its betterment will be greatly appreciated.

The editor, on behalf of the collaborators in this undertaking, desires to express his appreciation of the cordial reception tendered the previous volumes and sincerely hopes that the third edition will meet with the same friendly approval.

Allen Rogers.

Brooklyn, N. Y.
May, 1919.

PREFACE TO FIRST EDITION

THE purpose in preparing this book has been to assemble the ideas of a large number of men who are recognized authorities in their respective lines and thus produce a volume which would represent modern American methods and processes. It has been the aim of the authors not to give undue attention to minor details in order that the student may more fully appreciate the fundamental principles set forth. The subject matter is essentially descriptive without, however, omitting the theoretical considerations necessary for the proper understanding of the subject.

The editors ask the indulgence of the reader for any errors or omissions that occur in the present volume. In a work of this character, covering so wide a range, frequent revisions will be necessary, and they will be grateful for any suggestions with this end in view that may be submitted to them.

The authors' acknowledgments are due to the various manufacturers who have furnished cuts of their machinery; to Mr. George C. Abbe for his aid in the preparation of drawings; and to Mr. Charles M. Allen, who has given valuable assistance in the preparation of the manuscript.

ALLEN ROGERS, Brooklyn, N. Y.
ALFRED B. AUBERT, New York City.

MAY 1, 1912.

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Chief Biologist, Wahl-Henius Institute of Fermentology.

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Chemist National Fruit Juice Co., Lafayette, Ind.

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Consulting Chemist to the Textile Industries New York City.

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Professor of Chemistry, Lowell Textile School.

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Paper Expert, Norwood, Mass.

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Chief Chemist, Arlington Company, Arlington, N. J.

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Chief Chemist, National Gum and Gelatine Works, New York City.

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Professor of Chemistry, Kansas Agricultural College, Manhattan, Kansas.

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Jerome Alexander 1138

Chief Chemist, National Gum and Gelatine Works, New York City

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Clarence V. Ekroth 1156

Assistant Chief Chemist, Bureau of Foods and Drugs, New York City Health Department.

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Wahl Institute of Food Research, Chicago, Ill.

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INDUSTRIAL CHEMISTRY

CHAPTER I

GENERAL PROCESSES

ALLEN ROGERS

Grinding. In the manufacture of chemical products one of the most important operations is grinding. Not only must the raw material be reduced to a state of fine division before it can be used, but, in many instances, it must be placed on the market in the form of a fine powder or paste. The finished product depends entirely upon the nature of the material and its intended purpose. Thus, in many metallurgical operations it becomes necessary to crush very hard rocks or ores; whereas in the paint industry materials must be sold in a finely powdered form. There are, therefore, three general classes of grinding machines, namely: those which do crushing and coarse grinding; those which convert materials into a fine powder, and those which produce materials in the paste form. The following are some of the numerous types in use.

Jaw Crusher. The simplest and least expensive crusher is that known as the jaw crusher. It is a very heavy machine and consists essentially of a stationary steel plate against which a corresponding steel jaw works on a cam, imparting a rolling motion. This machine will crush the hardest materials. By means of an adjusting screw, the working parts may be regulated to give a coarse or fine product as desired. It finds application in metallurgical operations for ore crushing, in the manufacture of plaster of Paris, in the crushing of pyrites for sulphuric acid manufacture, and for various other purposes. Inasmuch as a great strain accompanies the working of this machine, it is always placed on a very solid foundation. Fig. 1 represents a small jaw

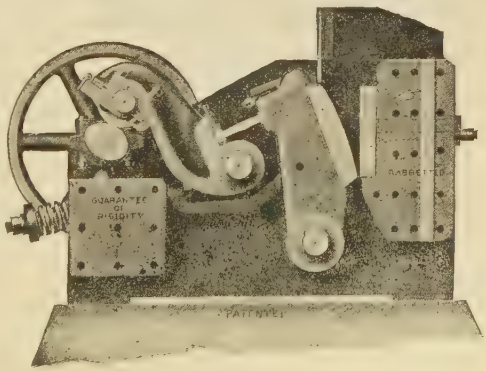

Fig. 1.

crusher for laboratory work. This may be either hand or power driven.

Fig. 2 illustrates a heavy machine for commercial purposes.

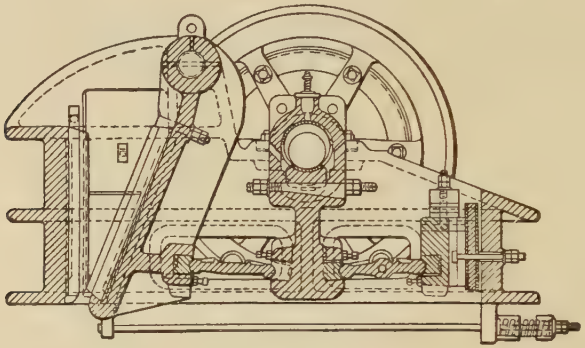

FIG. 2.

Crushing Rolls. This type of machine is employed quite extensively for reducing the product of the jaw crusher to a finer state of division, or for soft materials. Fig. 3 shows a laboratory roller, and Fig. 4 a heavy type of machine adapted to metallurgical operations, as well as to the crushing of soft materials. The rollers may be either plain or corrugated.

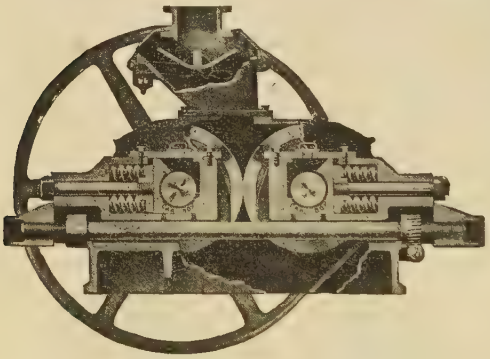

FIG. 3.

Rotary Fine Crusher. The rotary crushers are for rocks of moderate hardness. They are provided with double doors that carry all of the grinding parts and swing open as easily as the doors of a safe, thus readily exposing every part to inspection. Their capacity ranges from 2 to 30 tons per hour. By turning an adjusting screw, they may be regulated, while running, for fine or coarse work. See Fig. 5.

Disintegrator. This machine, known also as a pulverizing mill, is especially adapted for materials of a lumpy nature, like dry colors, soft pigments, borax, sulphur, starch, etc.; also for the mixing of dry materials like fertilizer. The construction of the machine is simple, as will be seen from Figs. 6 and 7. The steel cages run at a very high speed in opposite directions, thus driving the material through the steel bars by centrifugal force and pounding it to a powder. They are very strongly built, and may be very easily and quickly cleaned by taking off the top half of

the casing, removing the bolts holding bearing frames to the bed plate, then drawing frame and cages apart by tail screw, shown in the illustration.

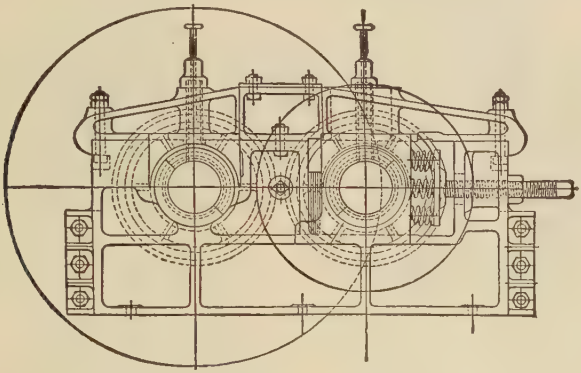

FIG. 4.

Chaser. There are various materials of such peculiar nature that they cannot be crushed by any of the machines described above. Such substances as seeds and drugs, for example, are best powdered by means of the chaser. This is also used for mixing loams in foundry work, for mortar, and for crushing and mixing in a semi-dry state. The chaser, Fig. 8, is equipped with a stone or steel bed on which rotate one or two "edge runners" or "travelers." An arm with scraper attached travels just in front of the runners and brings the material under the heavy rollers. The whole apparatus is set in a pan arranged with a gate for discharging.

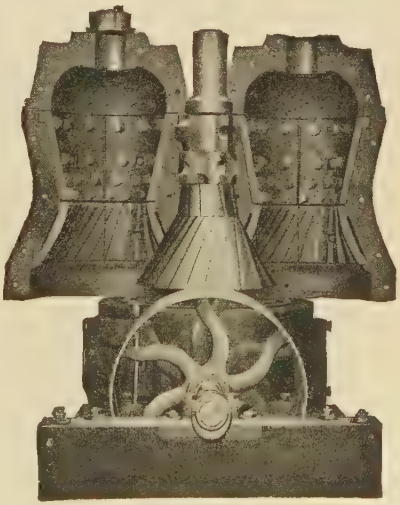

FIG. 5.

Buhr-stone Mills. For fine grinding of dry or wet materials stone mills are most common and are exceedingly well adapted to the purpose. Fig. 9 shows an under-driven dry mill, which is open in order to give an idea of the working surfaces. This mill grinds soft materials such as flour, pigments, and dry colors. Fig. 10 is the Ross improved paint and color mill ready for work. It is provided with a double set of stones having a water-cooling arrangement to prevent excessive generation of heat during the grinding of paste colors and paints. The material is fed in through the hopper and is carried by centrifugal force to the grinding parts of the first set of stones, from which it then passes to the

second set. The degree of fineness is regulated by means of set screws on the side. For paste and paint grinding it is necessary to provide a

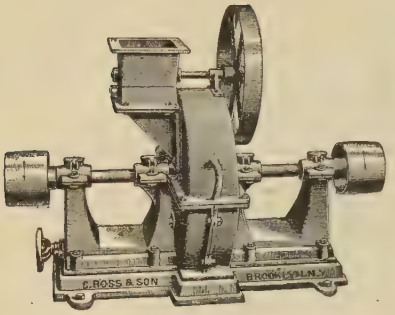

FIG. 6.

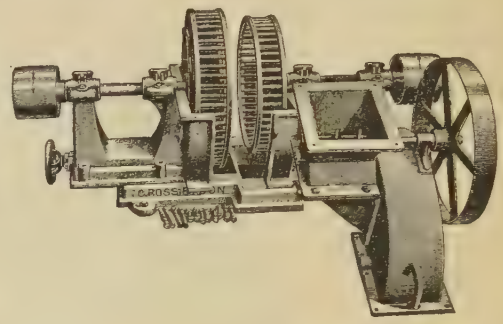

FIG. 7.

scraper on the traveling stone to remove the product as it passes the grinding face.

Ball Mills. These mills are on the market in several types for various lines of industry. Most common among them is the Fuller-Lehigh Pulverizer, Fig. 11, largely employed in the manufacture of cement. It consists of a horizontal ring or die against which revolve four balls

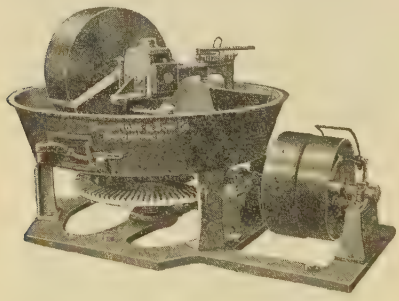

FIG. 8.

FIG. 9.

propelled by means of pushers. The die and pushers are chilled charcoal-iron castings, and the balls are of steel forgings. They revolve at a speed of about 155 revolutions per minute, and hence press against the die with enormous centrifugal force. The material to be ground is fed into the hopper, which in turn serves the feeder. The material discharged by the feeder falls down into the pan of the mill, situated below the die, and is drawn up from this in between the rapidly revolving balls and stationary die by means of air currents induced by fans placed in the

chamber above the die. The material is pulverized by the rolling of the balls against the die, the grinding action being similar to that of a mortar

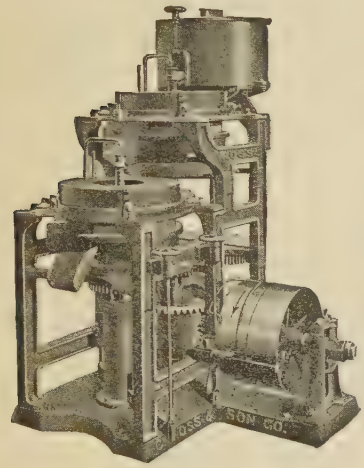

FIG. 10.

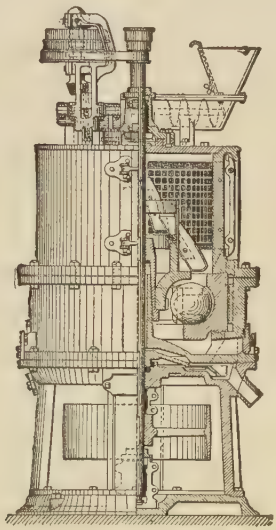

FIG. 11.

and pestle. The finely pulverized material is sucked upwards by means of the fans and out through the screens. The material passing through the screen falls down between this screen and the outer casing, and is dis-

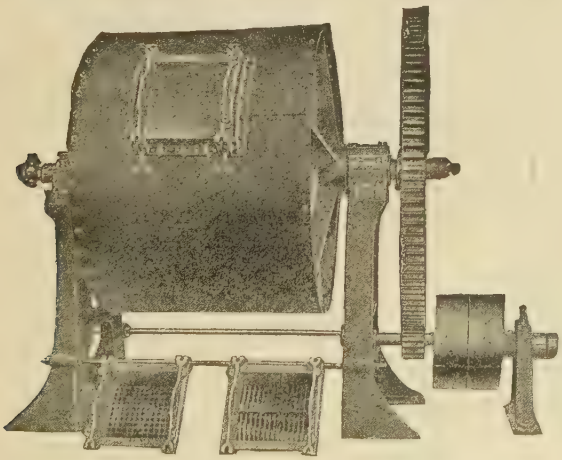

FIG. 12.

charged from the mill through the discharge spout, which may be placed at any one of four quarters of the mill. The feed to the mill, and consequently the fineness of the product, may be controlled in two ways, either by a slide on the hopper or by means of the stepped pulley connected to

the screw conveyor by gearing. The mill is provided with two screens, one, the inner, of 1-inch mesh made of very heavy wire to protect the outer one. The outer screen does not really screen, but merely controls the draft of air, and hence the fineness, since the greater the velocity the greater the carrying power of the air, and the coarser the product.

Pebble Mills. Pebble mills grind principally by friction due to the sliding, tumbling, and rolling inside the mill of a great number of flint pebbles or porcelain balls mixed with the substance to be ground, the movement being caused by revolving the mill at a regulated speed. As pebble mills are not crushers, all material should be crushed to a certain degree of fineness before it is charged into the machine. The mill shown in Fig. 12 is lined with vitrified porcelain, thus presenting a grinding surface which will neither contaminate nor discolor the material being pulverized.

Tube Mills. The general principle of grinding which operates in the tube mill is the same as in the ordinary pebble mill, the difference being that the material to be ground in the tube mill is fed in at one end and is delivered as a finished product at the other, the fineness of the product being regulated simply by the speed at which the material is fed into the machine. The slower the feeding the longer the material receives the action of the pebbles and the finer the discharged product. To make a coarse material, the feeding is increased.

Some of the more modern forms of tube mills are provided with a "Spiral Feed." By means of a crescent-shaped opening located where the spiral starts, a certain quantity of the material is allowed to enter, and, as the machine revolves, this travels forward until it reaches the center where it enters the grinding chamber. Thus, after two or three revolutions, there is a constant feed of a regular amount of material. From the grinding chamber the product passes through a perforated plate into a reverse spiral and is discharged thence from the center of the machine. In this way all labor of shoveling pebbles is avoided.

Harding's Conical Mill. The Harding Conical Mill, Fig. 13, is a device wherein the large crushing bodies arrange themselves at the largest diameter and decrease in size toward the outlet of the cone. Coarse material entering the mill is immediately subjected to the impacts of the largest grinding bodies, is subdivided, and, according to the division, passed along to the next zone of smaller grinders, and so on until the discharge end is reached.

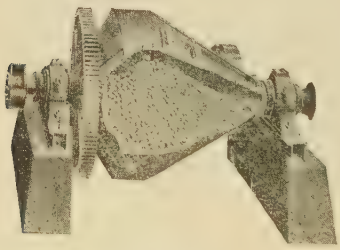

Fig. 13.

The grinding mediums automatically adjust or classify themselves to the work to be performed. An ideal Stage or Step Reduction is thus embodied within the single machine—a combination of percussion and attrition—comparatively a sledge hammer is used upon a spike, a nail hammer

upon a nail, and a tack hammer upon a tack, utilizing all the mechanical forces with the greatest possible effect.

Roller Mills. For the grinding of lithographic inks, colors in varnish, chocolate, and many other pasty materials the foregoing methods cannot be satisfactorily employed. The roller mill, Fig. 14, however, obviates the difficulties encountered and is largely used for the purposes mentioned. In its construction this machine usually consists of three steel rolls, which rotate at different speeds, thus passing the product to the front, where it is detached by means of a scraper and falls onto an apron. By means

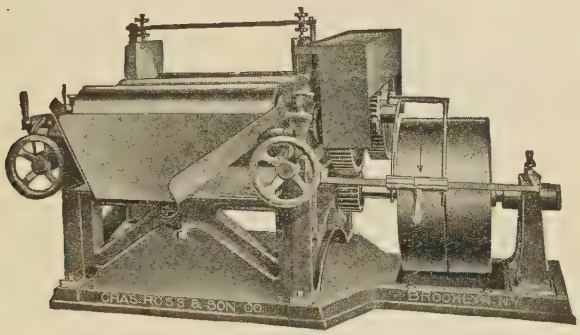

Fig. 14.

of adjusting wheels the front and back rolls are under perfect control and may be set to any degree of fineness desired.

Sifting. Often when the substance being treated is ground in a dry condition, it is necessary to separate the coarse from the fine particles. This is effected with sifting or bolting machines of numerous forms and styles. The degree of fineness is regulated by either wire sieves or bolting cloth. In all cases the ground material enters the reel, and, as this rotates, the fine powder passes through the meshes, leaving the coarse particles in the reel.

Sedimentation. To overcome the annoyance and loss caused by flying dust, many materials are ground in water. As the resulting turbid liquid comes from the mill it is allowed to flow into the first of a series of tanks, where the coarser and heavier particles rapidly settle, leaving the finer substance in suspension. The liquid is then drawn to the second tank, where it is allowed to remain somewhat longer than in the first tank. In each of the subsequent tanks the liquid remains for a longer period than in the one previous, thus giving various degrees of fineness to the resulting product, the coarse particles being returned to the mill for further grinding. This operation is sometimes spoken of as "levigation."

Filtration. This process means the separation of suspended solids from a liquid, and it often presents grave difficulties, especially when

working with large volumes. The medium of filtration may be paper, cloth, cotton, wool, asbestos, slag, or glass-wool, unglazed earthenware, sand, or other porous material.

Ribbed Filter. For handling small amounts of material the ribbed filter is very convenient and is made by folding an ordinary large filter in such a manner that, when inserted into the funnel, it will leave canals along the side. To prevent breaking of the filter the tip should be forced well into the neck of the funnel.

Bag Filter. A very satisfactory method of filtering coarse material is to arrange four pieces of wood as shown in Fig. 15, and on the brads suspend a piece of muslin in such a manner as to form a bag. The portion passing through at first may be slightly cloudy, but, as the pores fill with the precipitate, the filtrate becomes clear.

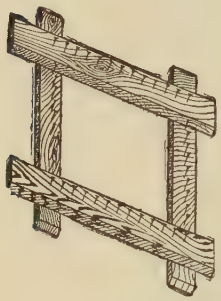

Fig. 15.

Suction Filter. This form of filter is used very largely where it is desired to retain the filtrate as well as the solid matter. It consists of a box arranged so that the lower section is connected with the vacuum pump, and over the perforated bottom is placed the canvas or other filtering medium.

Filter Press. A very rapid and convenient method of filtration is by means of the filter press. Although they are all built on the same principle, their details of construction vary to a marked degree. In its simplest form, however, it consists of dis-

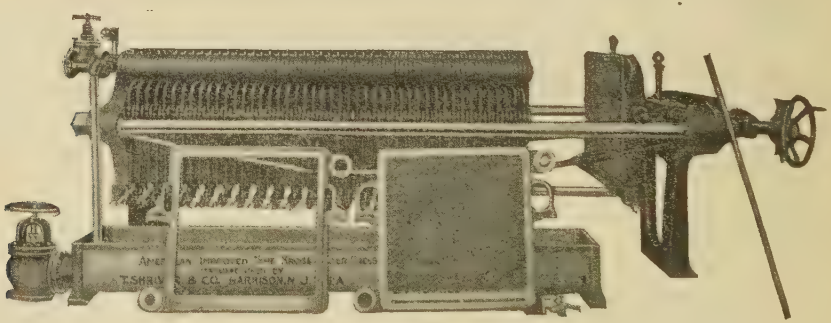

Fig. 16.

tance frames and plates, Fig. 16. These plates and frames rest upon a pair of parallel bars and are held in position by lugs projecting from each side. Over the surface of each plate is stretched a filtering medium, usually cloth, held secure by pegs; the whole being forced against the adjacent frame by means of a screw or hydraulic pressure. The material to be filtered is forced through the channel along the top of the press and

into the distance frames. The solid material is held back by the filtering medium, gradually filling the chambers and producing a solid cake. The liquid which passes through the filter is allowed to discharge into the channels along the lower portion of the press, where it may be recovered or discarded as wished.

A more recent form of filter press is the Sweetland self-dumping filter, shown in Fig. 17. The material to be filtered is forced into the filter body by gravity pressure or by means of a pump. The filter body comprises two semi-cylindrical castings of high tensile strength. As soon as the filter body is filled, the pressure rises, causing the liquid portion to pass through the filter cloth, while the solid matter is deposited on the leaf in a compact form. When the filter is full, the bottom half of the body is lowered, and then, by reversing the pressure, the cake is easily and very quickly detached.

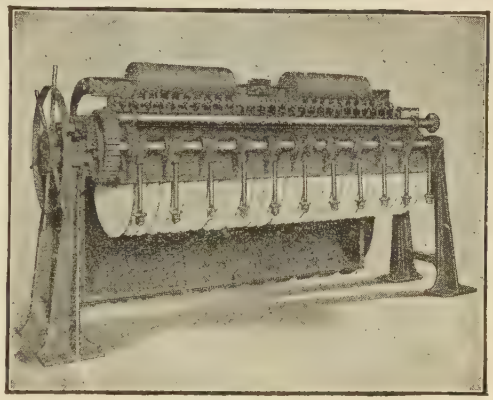

FIG. 17.

Open Tank Filter. This style of filter consists of a series or "basket" of filter cells attached to a common header, a movable hoisting device, and a series of two or more tanks. In operation the basket of cells is lowered into the first, or loading tank, where the liquid to be filtered is kept at a constant level and thoroughly mixed by proper agitation. Suction being applied, the clear filtrate is drawn through the filtering medium, leaving the solids deposited on the surface of the cells in the form of a cake. The basket carrying the adhering cake is now submerged in the washing tank, where sufficient wash water is drawn through to displace the filtrate occluded in the cake.

The basket is then lifted out of the washing-tank and held suspended long enough to permit the vacuum to draw out the excess wash water held by the cake. When ready to discharge, the basket is conveyed to the point of discharge and the cake blown off. The basket is now ready to re-enter the cycle of operation by returning to the loading tank. The size of tanks and their arrangement are made according to requirements. The size and style of filter cell will depend upon the capacity required and the character of the material to be filtered.

Rotary Filter. This form of filter (Figs. 19 and 20) consists of an open container in which is suspended a drum with periphery composed of a number of shallow compartments covered by a filtering medium.

Each compartment, by means of individual pipe lines, is connected to a perforated trunnion, which turns against a stationary valve cap, attached

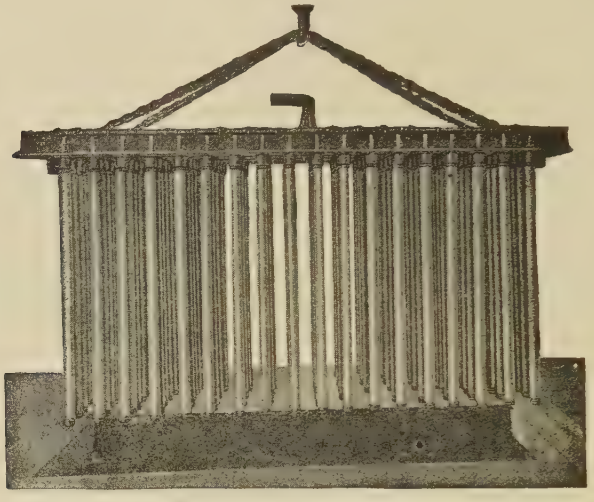

Fig. 18.

to suction and blow lines. The arrangement is such that suction and air pressure may be applied at different points to each of the compartments during every revolution of the drum. In operation the liquid is kept at a constant level in the container and thoroughly mixed by proper agitation. As the drum rotates slowly, suction is applied to the several compartments while they pass through the liquid to be filtered; the clear filtrate is drawn through the filtering medium, leaving deposited on the surface of the drum the solids in the form of a cake. As the compartments emerge from the container (suction being continued), the cake is subjected to a wash applied by means of a sprinkler equipment. Just before the compartments re-enter the container, suction is automatically cut off and air under pressure applied, causing the cake to discharge over an apron or " doctor " in the form of a continuous ribbon.

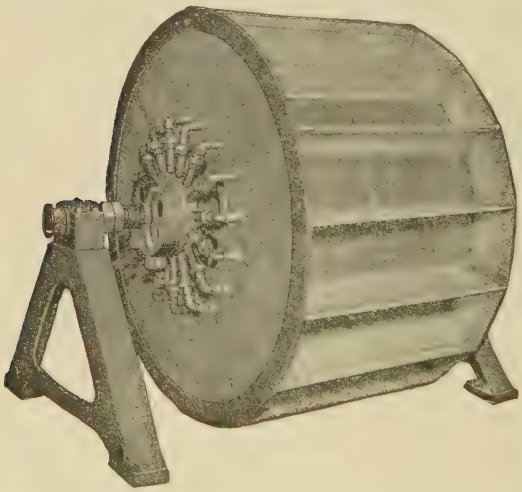

Fig. 19.

Where exceptional dryness of the cake is desired pressure jacks are set just above the point of discharge.

Although this machine may be manufactured in various sizes, the standard unit has a drum 6 feet in diameter, usually with a 5-foot face, a size conceded to be the most convenient for industrial filtration. The principal advantages of this type of filter are:

First—Continuous automatic operation.

Second—Elimination of manual labor.

Third — Cake formed, washed, and discharged during every revolution of the drum.

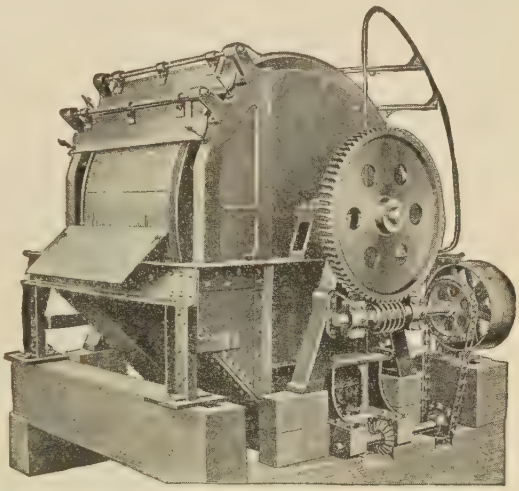

Fig. 20.

Centrifugal Machine. This appliance separates liquids from solids. It is especially adapted to the drying of crystals in that it throws off the

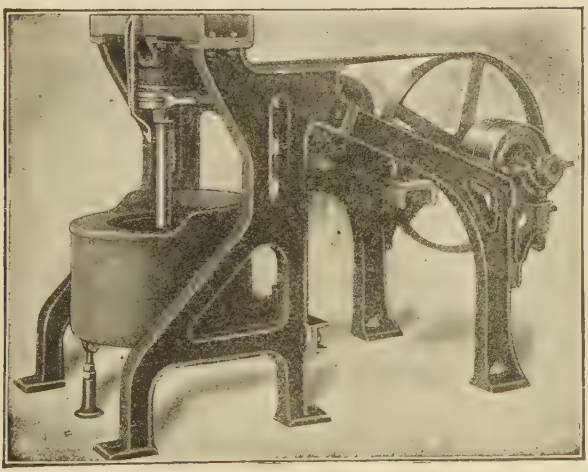

Fig. 21.

adhering mother liquor by centrifugal force. It is also employed for drying yarns, textiles, wood pulp, sugar, starch, etc. The centrifuge, therefore, is used more as a means of drying than of filtration. It consists of a cylindrical, perforated basket fixed to a vertical shaft, which rotates at a very high speed (900 to 1200 revolutions per minute), Fig. 21.

By means of the centrifugal force generated the contents of the basket are driven to the outer wall, where the solid material is detained and the liquid thrown off. In working with the machine great care must be exercised lest grave accidents occur. It is also necessary to see that the machine is carefully constructed. In some operations, such as for laundry purposes, or where there is an escape of fumes, it is very desirable to have an unobstructed top. See Fig. 22.

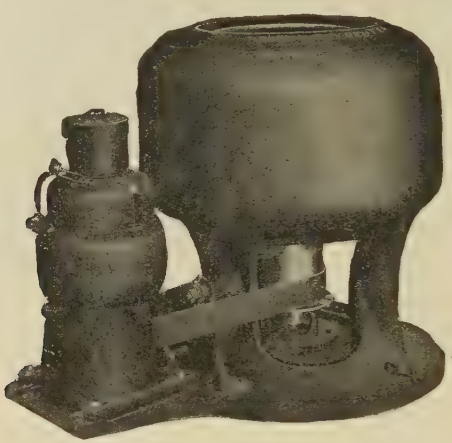

Fig. 22.

Drying. Before subjecting material to the drying process proper, it may be advantageous to remove as much of the adhering liquid as possible by draining, filtering, or centrifuging. The water that still adheres is then removed by evaporation in contact with the air at as high a temperature as is compatible with the substance and with economical practice. Whenever waste heat is available it should be used.

That the drying may be uniform, the substance to be dried is stirred, usually by mechanical appliances. The simplest arrangement would consist of a platform of metal or stoneware, heated by flue gases, and upon which the material would be spread and stirred from time to time; this is not, however, an economical process. A less wasteful method is by means of drying chambers built of brick, wood, or metal. The chamber may be heated from the inside, or the air passing through it may be heated. An exhaust or fan aids in the removal of the moist air.

Where temperatures of 100° C. or less are desired, the air may be heated by passing it over steam-heated coils, or the plate on which the material is placed may have a steam-heated jacket. Since the point where the heat enters the apparatus is the point of greatest heat, it is customary to convey the material from the further and cold end of the apparatus toward the hottest portion. For this purpose the shaft furnace can be used, provided

the material is hard enough and there is no need of regulating the temperature very carefully. A large number of more or less efficient forms of dryers are manufactured, among them vacuum dryers, which dry with considerable saving of labor, fuel, and time. Vacuum dryers may be divided into shelf dryers, for material that does not need to be stirred while drying; rotary dryers, for material which must be continuously stirred; and drum dryers for substances like glue, which readily acquires a dry film on the surface.

Vacuum Shelf Dryer. The vacuum shelf dryer, Fig. 23, is adapted to the drying of any material that can be handled in pans or trays, such as sheet and reclaimed rubber of all kinds, rubber compounds, paints, dyes, extracts, pastes, glue, soap, salts, albumens of all descriptions, starch, glutin, rosin, vegetables, fruits, sugars, small electrical apparatus, plates, chemicals, various by-products and liquid substances.

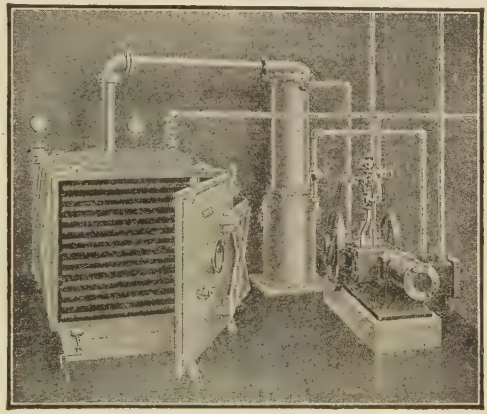

Fig. 23.

This dryer consists of a rectangular chamber containing hollow steam or hot-water-heated shelves, placed one above the other. The material to be dried is loaded in pans or trays which are placed on the shelves. The apparatus is then closed, the vacuum produced, and the drying commenced. If desired, the volatile matter or solvents removed from the material may be reclaimed. This type of dryer is used very extensively in many industries and is adapted to the drying of a large class of materials.

With the apparatus is furnished a vacuum pump and condenser, to produce and maintain a high vacuum during the drying operation. If the drying is to be done at an extremely low temperature, hot water is used as a heating medium, and the apparatus is supplied with a hot-water circulating system.

Vacuum Rotary Dryer. This dryer, Fig. 24, is used for drying semi-liquids and materials in granular form, such as reclaimed rubber, rubber compounds, chemicals, by-products, starch, cereals, fertilizer, dextrine, or any material that permits tumbling or mixing while being dried.

The dryer consists of a hollow, steam-jacketed cylinder fitted with heads at each end. In the center of the cylinder is a revolving heating tube carrying arms and paddles which effect a tumbling over or mixing of the material being dried. The dryer can be operated in connection with a barometric or surface condenser, depending on the amount of moisture

or solvents being drawn from the material treated and also on whether or not it is desired to reclaim them.

In operation, steam is supplied to the jacket of the casing and to the inner revolving tube. The space between the revolving tube and the jacketed shell, after being loaded with the material to be dried, is evacuated. This vacuum causes a rapid evaporation of the moisture and other solvents contained in the material. The vapors pass to the condenser where they are condensed and either thrown away or reclaimed as desired.

For drying most materials the outer casing consists of the construction above described, but for materials which tend to adhere to the shell, the outer casing is made of cast gun-iron, cast with a jacket between two shells. This construction permits the inside to be machined the full length and

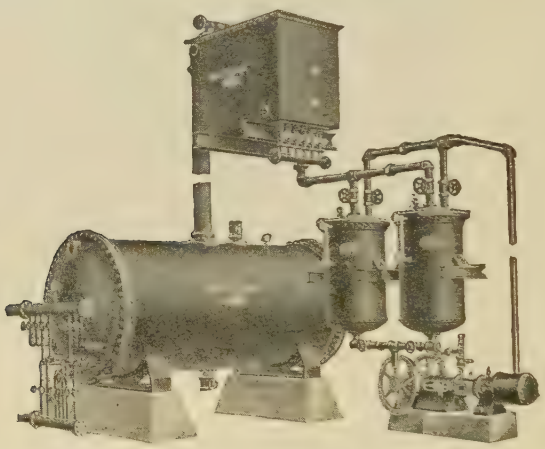

Fig. 24.

in such a way that the paddles or scrapers can be set close to the shell to prevent material adhering to it while drying.

For loading, the dryer contains one or more large openings at the top, which are fitted with cast-iron covers. When necessary, these covers are also supplied with an observation glass. The unloading apertures, one or more in number, are placed at the bottom of the shell and consist of doors, properly hinged and counterbalanced. The doors are flush with the inner shell of the dryer so that no material can lodge in the unloading apertures when the doors are closed. Most dryers will unload the charge in a few minutes, but for ease in loading and unloading, it is desirable to so place the apparatus that it can be charged from and discharged into hoppers that can be connected with conveying devices.

Vacuum Drum Dryer. This ideal apparatus (Fig. 25) for converting liquids into a dry powdered or flake form is used for drying solutions,

emulsions, and pulps, such as dyewood extract, quebracho, white lead, glues, milk, acids, chemicals, and other liquids containing solids. It consists of a hollow drum revolving in a sealed casing provided with devices for applying to, and removing from, the drum the material being treated, and for delivering the dry product to suitable receivers. The bottom of the chamber acts as a reservoir for the liquid. Agitators for mixing and coils for regulating the temperature of the material are provided when necessary. Steam or hot water is supplied to the interior of the drum. A high vacuum is maintained in the casing by means of a dry vacuum

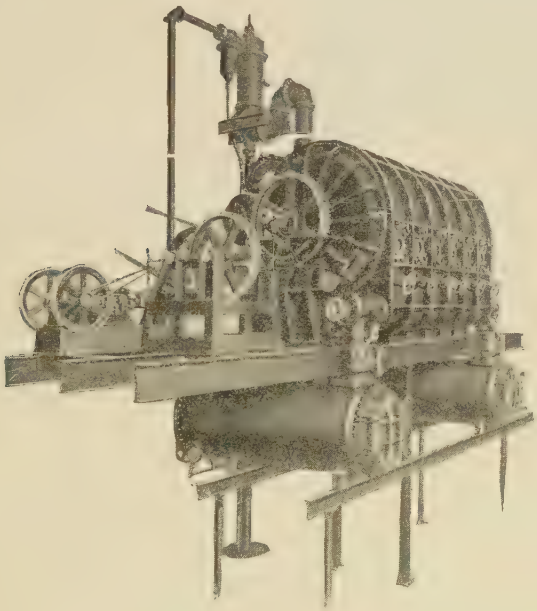

Fig. 25.

pump and the material is therefore dried at a low temperature. Moisture is removed by evaporation. A condenser is provided for condensing the vapors from the casing, and recovering them if desired.

The bottom portion of the dryer serves as a reservoir for holding a large quantity of the liquid material. There is ample space between the top surface of the liquid and the bottom of the drum to prevent foaming material reaching the drum. Agitators are provided for material requiring constant stirring. Coils are placed in the reservoir for heating or cooling the liquid when temperature regulation is desirable. The drum journals are supported in bronze bearings and are equipped with suitable stuffing boxes, steam and drain connections. Observation glasses are provided for noting the interior operation of the dryer. Ample space between the drum and the casing is afforded in the larger dryers to permit all interior

parts being thoroughly cleaned with a scrubbing brush and cleansing material.

For products which are removed from the drum in powdered or granular form, two receivers are usually provided to enable the dryer to be operated continuously, a conveyor being used to deliver materials to one receiver while the other receiver is being emptied. For flaky materials which cannot be readily conveyed a single large receiver is used and the drying operation suspended, while the dry product is being unloaded, and the vacuum again created in the emptied receiver.

While the vacuum drum dryer has, in theory, been considered the ideal apparatus for drying liquids, satisfactory commercial results were not attained until devices and methods for applying the liquid to the drum were perfected. Where the drum dips into the main body of the liquid, constant level cannot be maintained on many materials, due to the agitation and foaming of the liquid. This constant change in level makes a corresponding change in the amount of drum surface dipping in the liquid, which varies the moisture content in the finished product, interrupts the continuous operation of the dryer, reduces the output, and increases the cost of operation.

Lixiviation. The process of lixiviation separates water-soluble material from insoluble or less soluble material. The substance to be treated with water may be suspended in bags or baskets, or placed in tanks provided with perforated false bottoms. The solution, being denser than water, sinks to the bottom and may be removed. The material is usually submitted to a systematic treatment with water in such a manner that the pure water first comes in contact with the nearly exhausted substance, and then with the less exhausted in another tank, and so on until it reaches the last tank containing the fresh material. Such a series of tanks is known as a battery. The term *extraction* is generally used when solvents other than water are employed. It is possible to extract several substances from the original raw material by the successive use of several solvents such as water, alcohol, ether, and naphtha.

Crystallization. Crystals are geometric solids which form when a compound separates from its concentrated solution. The solubility of most substances increases as the temperature of the solvent, usually water, is raised. A limit may be reached, however, for every temperature when no more will dissolve, and the solution is said to be saturated. If the temperature be now decreased, crystals of the substance will separate, and these crystals, though formed in an impure mother liquor, may be quite pure. By evaporation or concentration of the mother liquor more crystals will result, which, however, will be less pure than the first crop. Thus, this operation may be continued until the impurities accumulating in the liquor become so great that the crystals will enclose a large amount of foreign matter. This difficulty can be prevented to a certain extent by stirring the solution while crystallization takes place and thereby causing

the separation of very small crystals, or crystal meal, which can then be washed so as to remove the adherent impurities. Fig. 26 shows a crystallizing pan used extensively in the manufacture of T. N. T. and for concentrating and crystallizing various products under atmospheric conditions.

A special feature of the crystallizer is the fact that the jacket is cast integral with the pan, as will be seen from the illustration. This eliminates all joints, bolts, and packing. The advantage of this construction is obvious.

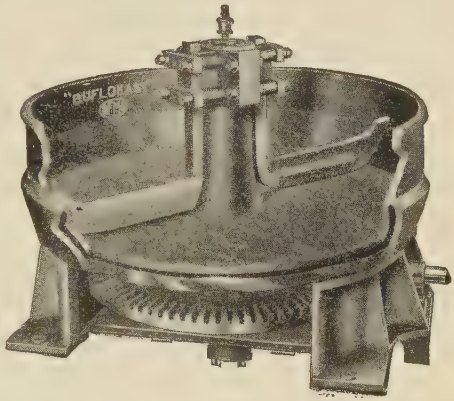

Fig. 26.

The crystallizer is used extensively in this country for evaporating the neutralized liquor of ammonia and nitric acid and drying and crystallizing the finished product. After the ammonium nitrate comes from this apparatus it is thoroughly dry. Steam is used in the jacket for concentration and cold water for crystallization. The device may also be used as an atmospheric dryer.

Fractional Crystallization. Crystals may be further purified by several successive recrystallizations. This method is for the separation of substances mixed in a solution; isomorphous substances or those crystallizing in the same system cannot, however, be separated in this manner. In such a case reaction upon the solution must so change the chemical composition of one of the substances that separation by crystallization becomes possible. An instance of this is the preparation of pure copper sulphate from a mixed solution of copper and ferrous sulphates. When blue vitriol is made from copper pyrites it is usually accompanied by more or less green vitriol. From this mixed solution only crystals of copper sulphate mixed with iron sulphate can be obtained, these salts being isomorphous. By oxidizing the ferrous to the ferric sulphate this may be avoided and pure copper sulphate prepared.

Calcination. In the process of calcination substances are submitted to the action of high heat, but not, however, to the point of fusion. Material may be calcined to drive off moisture, to drive off some volatile constituent, or cause a chemical action such as oxidation or reduction. The terms *roasting*, *firing*, *glowing*, or *burning* are sometimes used in place of calcination. The process is usually carried on in furnaces, of which there are three common types, *reverberatory*, *muffle*, and *kiln*.

Reverberatory Furnace. In the reverberatory or open roaster the material to be heated is exposed to the direct action of the fire gases. It consists essentially of an arched chamber built of brick and heated from

a grate placed at one end, while the products of combustion and reaction are removed by a chimney at the other end. The material is placed upon the bed of the furnace, the fire gases pass over it and are deflected by the arched form of the roof of the furnace so as to come more directly in contact with the charge. The inside of such furnaces is lined with firebricks, while the outside is built of common bricks.

If an oxidizing reaction is desired, that is, if the fire gases are to contain an excess of oxygen, such conditions may be produced by setting the fire bars widely apart and feeding the fuel in thin layers at a time. Should a reducing action be desired the fire bars must be placed closer together and the fuel charged in thick layers.

Muffle Furnace. The muffle furnace, closed or blind roaster, is built in such a manner that the fire gases do not come in contact with the substances to be calcined. It generally consists of a muffle of firebrick with the flues so arranged that the hot gases pass underneath the bed of the muffle and are then conducted over the top back to some point near the grate, where they are discharged into the chimney. A pipe is sometimes fitted to the top of the muffle, in order to discharge any gases which may be formed during calcination.

Revolving Furnace. It is frequently necessary to stir the material during calcination. If done by hand, this would entail much heavy labor. Mechanical means therefore have been devised, the most important of which is the revolver or revolving furnace. It consists of a drum or cylinder of iron or steel, Fig. 27, lined with refractory material and open at both ends. The drum, which may or may not be inclined, revolves slowly about its longitudinal axis, while the highly heated gases from the grate situated at one end pass through it. The hot gases leaving any of these furnaces may be economically used for drying or evaporating.

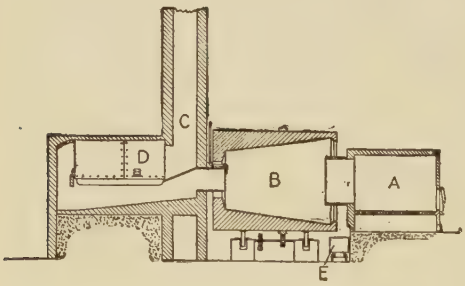

FIG. 27.

Kilns. Kilns or shaft furnaces may be periodic or continuous, and are very largely used in the burning or calcination of limestone. In periodic kilns the calcined charge is allowed to cool, then withdrawn, and the kiln recharged with fresh material. In the continuous form, the calcined material is drawn from the bottom at the same time that a fresh charge enters the top, the operation being a continuous one.

Evaporation. By evaporation is understood the conversion of a liquid into a vapor for the purpose of recovering any solid matter which may be dissolved in it. In most instances the liquid to be evaporated

is water, as other liquids would be recovered, and the process would be termed *distillation*.

Spontaneous Evaporation. This method is usually conducted in the open air by exposing the liquid in large shallow pans. The time required depends entirely upon atmospheric conditions, the best results being obtained on a windy day in hot, dry weather.

Evaporation by Direct Heat. By this method the flames or hot gases may play directly on the bottom of the containing vessel, or they may be made to pass over the surface of the liquid. In the former case the usual method is to employ large shallow pans so arranged as to be heated by the waste gases from other operations. In the latter mode of evaporation, the flue dust and ashes are very apt to fall into the pan, thus causing the product to become impure. This method is used, however, to some extent where the purity of the product is not essential.

Evaporation by Indirect Heat. Steam is very largely used for the reason that it is convenient to handle, and there is no danger of injury to the product by overheating. The simplest way is to circulate the steam through coils of pipe arranged inside the vessel. This method is especially adapted to the heating of liquids contained in wooden tanks. The temperature to which the liquid may be raised depends wholly upon the steam pressure, the latter being regulated to suit the conditions required.

Steam-jacketed Kettles. The most convenient method of applying steam is by means of the steam-jacketed kettle, Fig. 28. In conducting an evaporation the drain-pipe valve is opened to permit the escape of the first condensations, and to prevent bumping. The exhaust valve is then opened, the inlet valve given a half turn, and then slowly opened until a good supply of dry steam issues from the drip. The drip is finally closed and the inlet of steam so regulated as to secure the proper heat for evaporation. The kettles in common use are constructed of copper or cast-iron, the jacket usually covering one-half of the kettle. For purposes where copper or iron would not resist the action of acids or other chemicals it is customary to use a kettle lined with an enamel of easily fusible glass. Whenever it is necessary to stir the liquid being evaporated, the kettle is generally equipped with an agitator provided with paddles of various shapes.

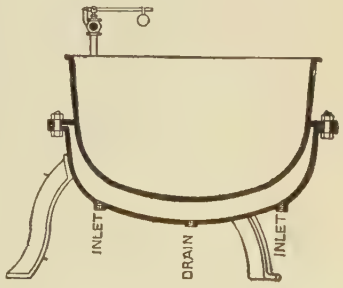

FIG. 28.

Evaporation under Reduced Pressure. There are many forms of apparatus for evaporation under reduced pressure, yet they all depend upon the same principle.

Vacuum Pan. The necessary equipment for this installation is a

vacuum pan, condenser, receiver, and pump. The vacuum or strike pan, Fig. 29, is a cylindrical vessel, *A*, usually of cast iron, having a dome-shaped top with vapor pipe, *B*, and a conical bottom provided with a strike or discharge valve, *C*. The pan is equipped with large heating coils of copper, and steam and vacuum gauges, also sight glasses, *D*, for watching the progress of the work, and proofstick for drawing test samples. The steam enters a manifold, *E*, from which it is distributed to the coils; each of the latter has a stop valve for steam, and drainage connections for condensation water. The vapors from the boiling solution pass through a save-all, *F*, connected at the bottom with the pan, where they expand and meet baffle plates, so that material entrained with the vapor may be returned to the apparatus.

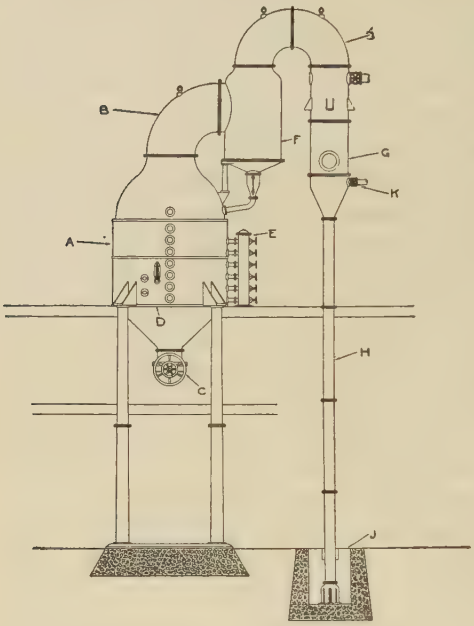

Fig. 29.

The vapors from the evaporating liquor pass into a condenser, *G*, in which they meet a shower of water. The incondensable gases are led off through a pipe, *K*, from the lower part of the condenser to a vacuum pump. The condensing water and water of condensation are carried off through the "leg pipe" or torricellian tube, *H*. The foot of the leg pipe is sealed with water in the hot well, *J*. On the dry system a receiver is used to which is attached a vacuum pump. In many cases, however, it is not necessary to collect the liquid which passes off, so that, on the wet system, it is possible to dispense with the condenser. A wet-system pump is so constructed as to take care of all condensations without the aid of this extra condenser.

Another form of single-effect evaporator is illustrated in Fig. 30, which shows a Zaremba single-effect pan.

Multiple-effect System. The most efficient method of evaporation is by means of the multiple-effect system. The apparatus usually consists of three or four vacuum pans, so arranged that the steam from the first pan passes through the coils or jacket of the next in line, and the steam generated in the second serves to heat the liquid in the third. The vacuum maintained in each of the pans increases as it approaches the pump for the reason that the condensations play quite an

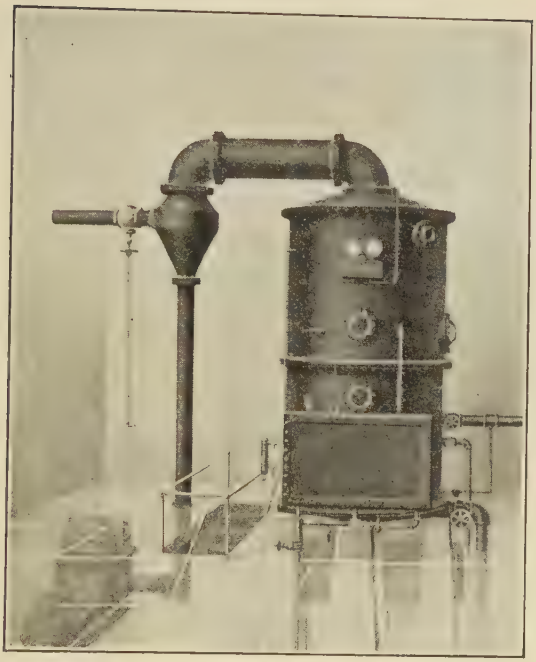

FIG. 30.

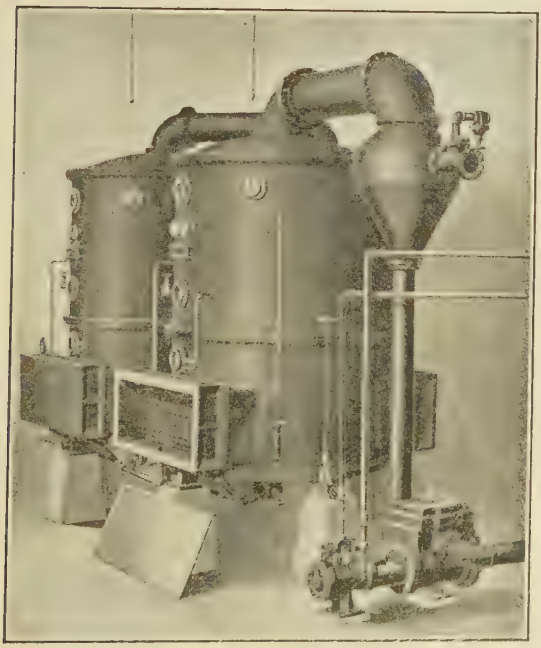

FIG. 31.

important part in producing reduced pressure. Thus it is that the pan having the highest temperature has the least vacuum, and that having the greatest vacuum has the least temperature. As a rule only three pans are employed, being known as triple-effect, although sometimes four are used and are known as quadruple-effect. Inasmuch as the boiling-point of the liquid varies with the pressure to which it is subjected, it follows that by proper adjustment of the pressure we can secure a corresponding adjustment of the boiling-point, placing it at will anywhere between certain practical limits. The lower limit is fixed by the cost of securing a good vacuum, and runs ordinarily about 125° F.; the upper limit is fixed by the temperature of the steam used, which for exhaust steam runs about 225°.

Zaremba Evaporator. Fig. 31 illustrates this type of evaporator and shows the apparatus set up and ready for work. Fig. 32 shows a layout

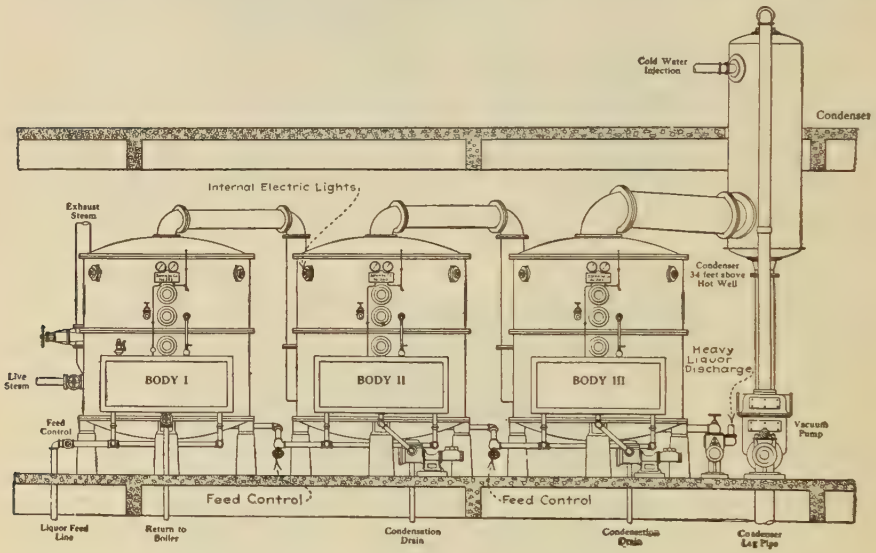

FIG. 32.

of the same form in triple-effect; while Fig. 33 shows a cross-section of one effect. In operating this form of evaporator the liquid passes into the first effect, where it becomes heated from the direct steam of the boiler. The steam thus generated passes to the coils of the second effect and thus becomes the heating medium. The steam from the second heats the coils of the third effect, which is in direct connection with the vacuum pump. The reduced pressure in the first and second effects is due to condensation. The liquid being evaporated is pumped from one effect to the next by means of a centrifugal pump.

To get a clearer understanding of the operation, suppose we had three single-effect evaporators, *A*, *B*, and *C*, of the same size, each with an inde-

pendent surface condenser and air pump. *A* takes exhaust steam at a temperature of 225° and delivers its vapor to condenser *A* at 195°. *B* takes steam at 195° and delivers its vapor to condenser *B* at 165°. *C* takes steam at 165° and delivers vapor to condenser *C* at 125°. In this case, excluding radiation and other losses, we would require for each pound of evaporation one pound of steam to produce the vapor, and about 25 pounds of cool water to condense it. But why not simplify our apparatus by rearrangement as follows: Eliminate condenser *A* and substitute for it the heating surface of single-effect *B*, that is, let the vapor from single-effect *A* take the place of the 195° steam previously fed into single-effect *B*. In like manner let the vapor from single-effect *B* be condensed in the tubes

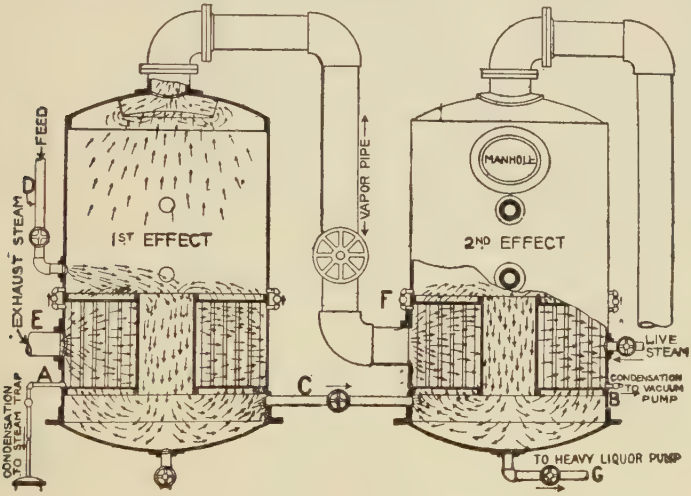

FIG. 33.

of single-effect *C*, while the vapor from the latter is condensed in condenser *C* as before. With this method of operation the temperature difference in each effect is the same as before, so also is the amount of work done, but we are feeding steam into effect *A* only, and injecting cold water into condenser *C* only, and are using but one-third as much of each as in the first case. Furthermore, we have discarded condensers *A* and *B*, together with their respective vacuum pumps. With this arrangement we are working under the multiple-effect system, that is, we have converted our three single-effects into one triple-effect, thereby increasing our evaporation to 3 pounds of water per pound of steam used, and decreasing our water consumption from 25 pounds to about 9 pounds per pound of evaporation, the amount of evaporation produced being practically the same in both cases. The theoretical steam economy of the multiple-effect, as stated above, is modified by a number of conditions, chief among which is the initial temperature of the liquor fed and the disposition made of the heat contained in the condensation from the various bodies. Ordinarily

the number of effects used does not exceed four, but for special purposes as many as seven or eight effects can be used advantageously; it all depends on the circumstances.

The pumps necessary for operating the multiple-effect consist of a vacuum pump for removing the air and other non-condensable gases from the condenser, a tail pump to withdraw the finished liquor from the evaporator, and condensation pumps to draw away the condensation from the steam chests operating at less than atmospheric pressure. Inasmuch as the steam exhausted by these pumps is used in the evaporator, their operation costs practically nothing. Under such circumstances, to use motor-driven pumps means a loss in economy.

All forms of vacuum apparatus call for the use of a condenser in which the vapor coming from the last pan is condensed by contact with cold injection water. In the wet system the air and gases present are entrapped in this warm mixture of condensed vapor and injection, the entire mass being withdrawn from the system by a wet vacuum pump and discharged. In the dry system of condensation, the condenser is made much larger and is mounted sufficiently high to allow the water discharged to flow into the hot well by its own weight against the pressure of the atmosphere. In this case air and non-condensable gases only are handled by the vacuum pump. In the surface condenser, which is practically a reversed evaporator, the vapor is confined to one chamber and the cooling water to another, being separated from each other by a tubular brass cooling surface.

As a rule the amount of water required varies from 25 to 30 pounds per pound of vapor condensed. One of the great advantages of the wet system lies in the fact that such a condenser can generally be made to draw its own supply of injection water from a neighboring stream or tank. The dry system requires a circulating pump. There is a large supply of warm water at about 110° F. coming from the condenser, which can frequently be used to very good advantage. The first pan delivers a quantity of distilled water at 212°, equal to the amount of steam used; this is preferably returned to the boiler. From the condensation pumps another supply of warm water is obtained at a temperature between the two former. The steam pressures ordinarily carried vary from 5 pounds down to atmospheric pressure; the vacuum from 23 to 26 inches.

Lillie Evaporator. The mode of operation which distinguishes the "Lillie" from other evaporators is that the results obtained are due to film evaporation; that is to say, the liquid flows over the heated tubes rather than through them, thus exposing a very large surface for evaporation. In the older forms of multiple-effect apparatus some difficulty was encountered from liquids depositing heavy incrustations upon the heating surfaces. This difficulty, however, has been overcome in the new model. The new feature, which corrects this condition, is the reversal at will of the direction of the course of the vapors or heat through the multiple-

effect, thereby making coolest what before the reversal was the hottest effect, and what was the coolest, the hottest. Fig. 34 shows a vertical longitudinal section through the body of the evaporator. The evaporating tubes slightly incline downward to the steam end and open through the heavy tube plate partition in which they are firmly expanded and by which they are supported. The other ends of the tubes are closed except for a small air vent in each. They are not fastened or supported in any way, and the tubes are quite free to expand or contract independently of the shell of the effect.

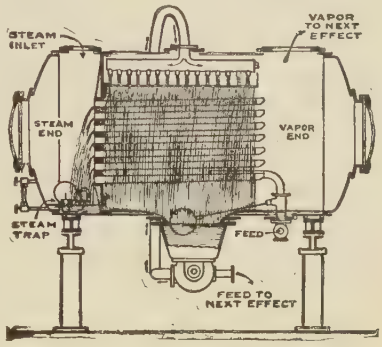

Fig. 34.

On the under side located midway between the ends of the evaporator is a centrifugal circulating pump. The condensation from the steam in the tubes flows back into the steam end, and thence through a steam trap into the end of the next cooler body, and finally to the atmosphere from the coolest body, in the case of the multiple-effect. The solution delivered by the centrifugal pump is forced on to a perforated distributing plate, from which it flows over the tubes in a deluging shower. The circulation in this case is independent of ebullition, and there being no depth of solution on the tubes, the vapors have a free passage for escape.

Standard Swenson Horizontal Tube Evaporator. As will be observed in Figs. 35 and 36, the Standard Swenson is a rectangular evaporator with horizontal tubes located near the bottom of each effect. It is made up in sections of heavy cast-iron plates with machined and drilled faces or flanges. The assembled castings are bolted together against suitable packing material (usually sheet asbestos) making a vacuum-tight joint. There is a steam chest at each end cast as an integral part of the vertical tube sheets. Each tube passes well through both tube sheets and is packed in by plates and rubber gaskets. This scheme of packing makes possible the use of any material or gauge of tubing the requirements demand, and as a matter of ease of renewal has proved a source of great satisfaction, and has extended the use of the evaporator enormously. Unlike other attempts at tube packing it combines vacuum tightness and resistance to high temperature with the utmost ease of removal. The economy both as regards steam and condensing water required is directly proportional to the number of effects. Over 90 per cent of the evaporators in operation to-day use nothing but exhaust steam as a source of heat for evaporation, whereas live steam (in much greater quantity) would be necessary with open-pan boiling. This is only possible because of the reduced pressure or vacuum that is maintained in each evaporator unit or effect.

Each effect of an evaporator is really a condenser in which the material

being concentrated acts as the condensing agent. A given weight of steam, if condensed, will evaporate approximately an equal weight of water (practically 95 per cent in a well-covered equipment), provided the pressure in the space surrounding the material being concentrated is lower than in the steam space. This is the basic principle of all evaporators, and in order to bring about the multiple use of the latent heat that is given up when the steam or vapor is condensed, each succeeding effect is operated under a lower absolute pressure. The steam that is condensed in the first effect produces approximately an equal amount by weight of vapor from the solution being concentrated, and this vapor goes to the second effect, is condensed, and in turn produces another equal quantity of vapor also

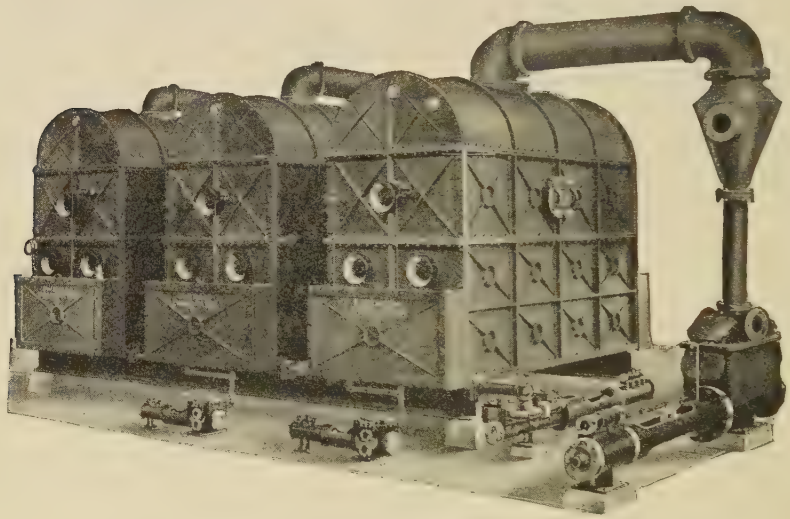

Fig. 35.

from the solution being concentrated, which goes to the third effect and so on through the remaining effects. In this way the latent and some of the sensible heat is used as many times as there are effects. For example, 1 pound of steam used in the beginning will remove in practice about $3\frac{3}{4}$ pounds of water in a quadruple effect.

The number of effects to use depends entirely on conditions as regards quantity of exhaust available, boiling properties of solution, and cost of coal as compared with cost of equipment. Some materials have boiling properties that limit the equipment to a double or triple effect, and others can be handled satisfactorily in sextuple units. As a rule, a quadruple effect is the limit of economy when coal cost, interest, depreciation, etc., are properly considered.

The number of effects in use usually has no bearing whatever on total capacity, as a single effect of a given size will in most cases do just as much

work, for example, as a quadruple effect having individual effects of equal size, but the quadruple effect, costing about three times as much, will

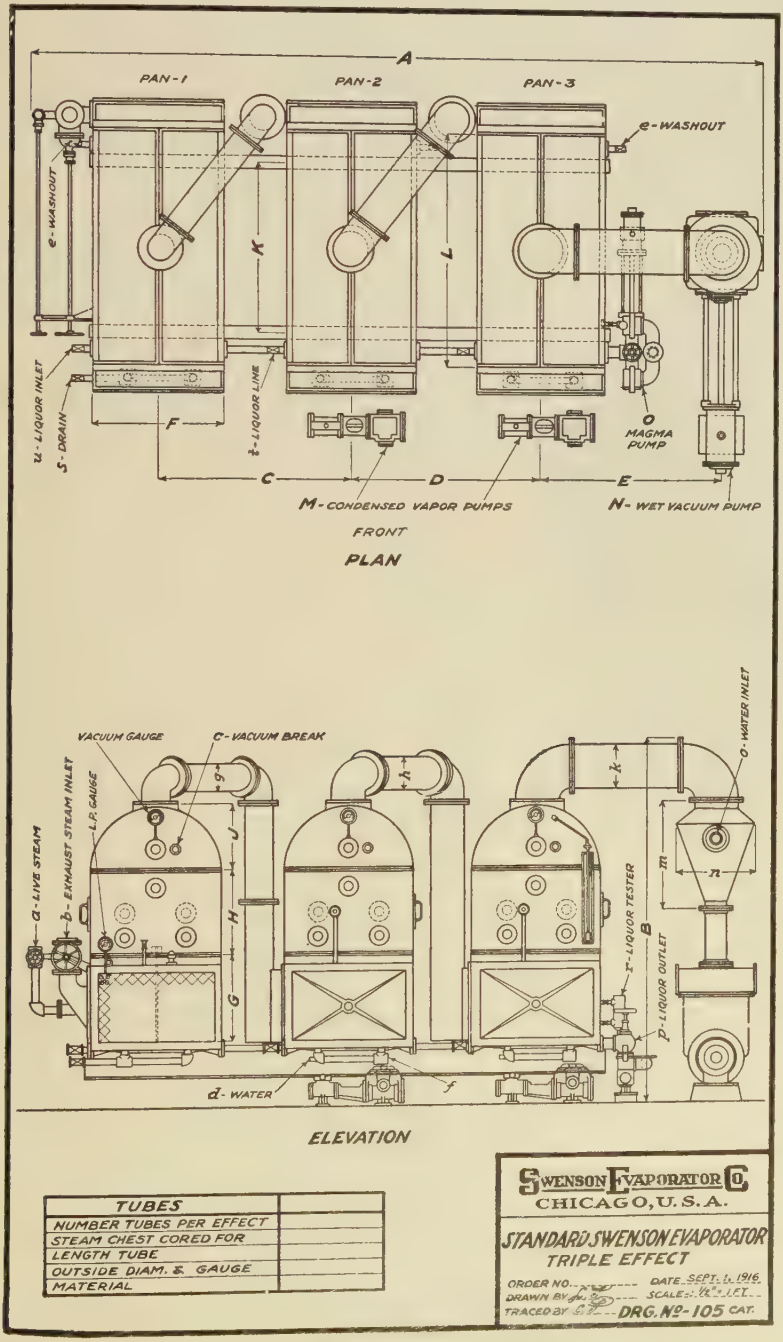

FIG. 36.

only use one-fourth as much steam and condensing water to accomplish a given evaporation. The reason for this is that the capacity of any evaporator is directly proportional to the effective temperature difference between the steam supplied and the vapor condensed in the condenser, which is always needed so as to produce a high vacuum in the last effect. The temperature range in a single effect is the same as the range between the steam used in the first effect of a quadruple and the vapor produced in the last effect, so that the capacity of both machines is the same disregarding radiation losses and excess boiling temperatures.

Zaremba Crystallizing Evaporator. This form of apparatus, Fig. 37, is especially designed for the concentration of crystallizing solutions, and the removal of the precipitated crystals without interfering with the process of evaporation.

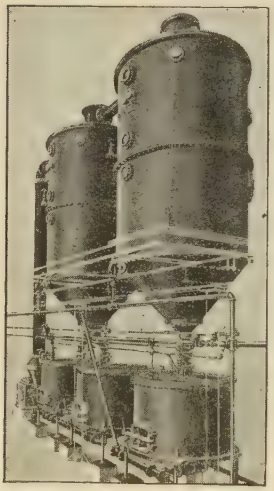

Fig. 37.

The weak liquor enters the first effect (in foreground) at top of cone and flows to the base of the steam-chest. By the action of the vapor generated in the tubes and the pressure exerted by the liquor in the downtake, a vigorous movement is set up within the tubes (about 30 feet per second), inducing rapid heat transmission and effective scouring action on the tube interiors. Owing to the large area of the downtake, the return flow to the bottom of the steam-chest is very slow (about 3 feet per second or less), allowing the crystals formed during the concentration to separate from the liquor and drop gently into the zone of unagitated liquor contained in the cone. The heavy liquor carrying these suspended crystals flows out through the plug cock at tip of cone and into the salt filter.

A liquor line connects the bottom outlet of the filter to the liquor inlet of the second effect, which, being under a higher vacuum, draws the liquor through the filter and into itself by suction. The suspended crystals are left behind on the filter screen, where they are allowed to accumulate until the salt filter is filled (determined by sight glass). The connection between evaporator and filter is now shut off by closing the plug cock between, and, after drawing off the heavy liquor, the contents of filter are washed with weak liquor, hot water, and steam. The connection to the second effect is then closed, the discharge door of the filters is opened, and the thoroughly washed crystals are removed in an approximately dry condition.

After the filter has been emptied its door is closed and the contained air removed by replacing it with steam. The condensation of this steam

soon produces sufficient vacuum to pull the mixture of liquor and salt collected in the cone down into the filter when the plug cock is opened. The liquor level in the evaporator is again brought to standard height and the filter placed in circuit by opening the connection to the next effect. Where the amount of salt precipitated is comparatively large, two filters are attached to one evaporator body, thus making it possible always to have one filter connected to the evaporator, inasmuch as the filters are used alternately. By either arrangement the salts are washed and removed without interfering with the work of the evaporator above. If desired, the crystals can be dissolved within the filters and the saturated solution removed by pumping.

These evaporators consist of two parts: (1) The evaporator body, in which the evaporation occurs; (2) the salt filter underneath, by means of which the precipitated crystals are separated from the concentrated liquor, washed clean, and removed from the system.

The shell of the evaporator body is built of heavy cast-iron or steel. Its lower portion, below the heating surface, consists of a cone into which the salt is precipitated and funneled into the salt filter below. Mounted within the shell immediately above the cone is the cylindrical steam-chest, fitted at top and bottom with dished heads of steel into which 2-inch charcoal iron tubes are expanded. The fastening of steam-chest in shell is effected by means of a special design giving no opportunity for trouble. Copper construction is used for corrosive liquids

The downtake is an annular opening, widest at the bottom, extending entirely around the steam-chest. Circulation of liquor is upward through the tubes, outward toward top of downtake, downward between steam-chest and exterior shell, then inward to lower end of tubes. This action produces a ready separation of the salt crystals from the boiling liquor, throwing them into a zone of quiet in the conical bottom and thence into the salt filter.

The filter consists of a cylindrical chamber fitted with a filter screen placed close to the bottom. At the front and immediately above the screen is a swinging door through which the separated salt is removed. The conditions inside can be observed through the sight glass. Wash water is introduced through perforated pipes mounted under the top cover of filter. Suitable vacuum and liquor pumps are connected to the system to provide for all requirements.

The method of operation in the second effect is the same as has been described, except that the heavy liquor is drawn from the filter by the suction of a pump. The liquor discharged from this pump is either returned to the second effect to be recirculated or, if the final density has been reached, it is discharged as finished liquor.

These evaporators are built either as single, double, triple, or quadruple effects, and are generally connected in such a manner that any one of the bodies can be cut out of service without interfering with the others.

Owing to the fact that each body of a multiple effect operates at a different temperature, it is frequently possible, by proper manipulation, to make a separation of salts where several compounds are present in the solution. Ordinarily, the weak liquor is fed to the hottest body and is finished in the coolest body, but for some purposes the flow of liquor is reversed, thus giving what is known as the " countercurrent " system of working.

By installing a preheater for feed liquor a substantial reduction in the amount of steam used is possible. They cost comparatively little and save much. All evaporators are equipped with internal separators, which makes impossible the carrying over of liquor by entrainment as a result of careless operation. Entrainment loss in this apparatus is thus reduced to the vanishing point.

The steam pressure used varies all the way from atmospheric to 60 pounds or more, depending on the circumstances. Ordinarily, direct-acting pumps are furnished, their exhaust being delivered to the evaporator. The condenser often can be so located as to draw its own water by suction.

Distillation. This operation is usually for the purpose of separating liquids from other liquids, or from solids, and may be considered as a special form of evaporation. In fact, evaporation and distillation are often carried on simultaneously. Many forms of distilling apparatus are in use, although they all have three points in common: (1) The still or vessel holding the liquids to be heated, (2) the condensers or cooling apparatus, and (3) the receiver or vessel in which the distilled liquid collects. Between the still and condenser is a spray catch, provided with baffle plates, which prevents any of the solution from being carried over mechanically by the vapor. The liquid is thus returned to the still while the vapor passes along to the condenser. The apparatus shown is made of copper, the condenser worm being tin-lined.

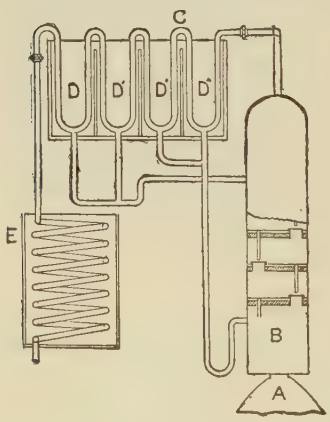

Fig. 38.

Column Still. The illustration, Fig. 38, represents one of the types of column stills in common use. The column or *dephlegmator* (*B*) is placed on top of the boiler (*A*) and is divided into chambers by means of plates, each of which has a dome or flat-covered opening, with an overflow pipe leading to the chamber below. The vapor from the boiling liquid passes up through the opening, where it bubbles out through the liquid on each plate. The heavier liquid which is condensed here flows down through the overflow pipes and into the boiler. Between the column and the condenser (*E*) is a series of U-tubes surrounded by a water-bath, which may be kept at any temperature desired. As the mixed vapors pass through these

tubes, the high-boiling portions are condensed and returned to the column, while only the lightest or more volatile liquid passes through the coil in the condenser (*E*).

Coffey Still. This still (Fig. 39) consists of two towers, (*A*) known as the *analyzer*, and (*B*) the *rectifier*. Free steam is forced into *A* through the pipe (*C*), where it bubbles up through the liquid on the preforated plates (*D*) and out by the way of (*E*) into the rectifier (*B*). The liquid to be distilled is now pumped through the pipe (*F*) and the coil (*G*), and is delivered into the analyzer by the pipe (*H*). The liquid in this way becomes heated by the steam surrounding the coil and is delivered hot to the analyzer. The hot liquid as it falls on the perforated plates spreads out in a thin layer and runs down to the next compartment through the overflow pipe (*J*). The steam, passing up through the layers of liquid, heats it very hot and carries the volatile portion over into the rectifier. During the passage of the mixed vapors up the rectifier the steam becomes condensed by contact with the cold pipes, thus allowing the more volatile portion to pass out through the pipe (*K*) to the condenser (*L*). The water which collects in the bottom of the rectifier is pumped to the top of the analyzer through the pipe (*M*). From the bottom of the analyzer is a pipe (*N*) to act as a discharge for the spent liquor which has lost its volatile matter.

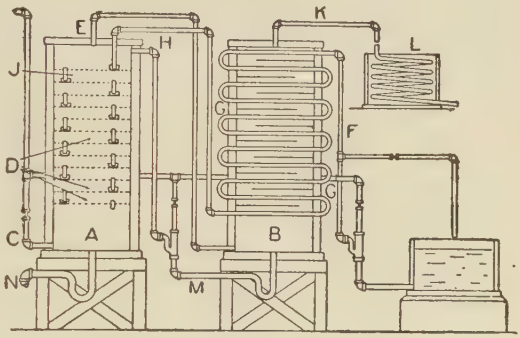

Fig. 39.

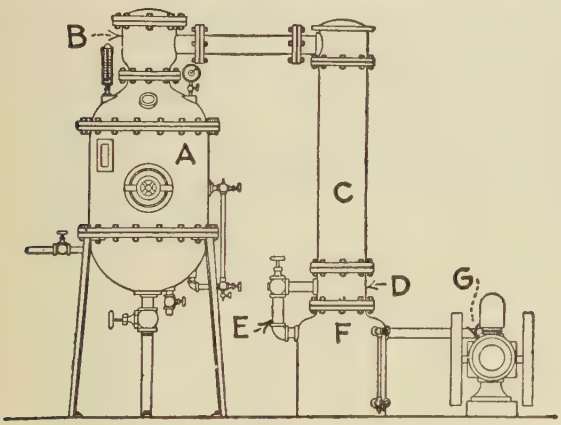

Fig. 40.

The foregoing apparatus is general in character and the principles involved may be applied in other lines of industry. In Chapter XXI the writer describes several types of stills as used in the distillation of coal-tar products.

Lummus Vacuum Still Outfit. Fig. 40 shows a vacuum still with

condenser and vacuum receivers. The still (*A*) is surmounted by a vapor bonnet (*B*), which acts as a baffle to any spray of unvaporized liquid that may tend to pass over into the condenser (*C*), which may be of either the coil or tubular type. After the vapor is condensed, it flows through the receiver (*D*) and pipe (*E*) into the vacuum receiver (*F*). When this receiver is filled, it may be emptied without destroying the vacuum in the still and condenser by closing the valve in pipe (*E*) and allowing the condensate to accumulate in (*D*). As soon as the receiver (*F*) has been emptied, the valve can be opened and the condensate will again run through to the large receiver. In cases where the recovery of the vaporized portion of the liquid is not required, the vacuum receivers may be dispensed with and the liquid or vapors be drawn off directly through the vacuum pump (*G*).

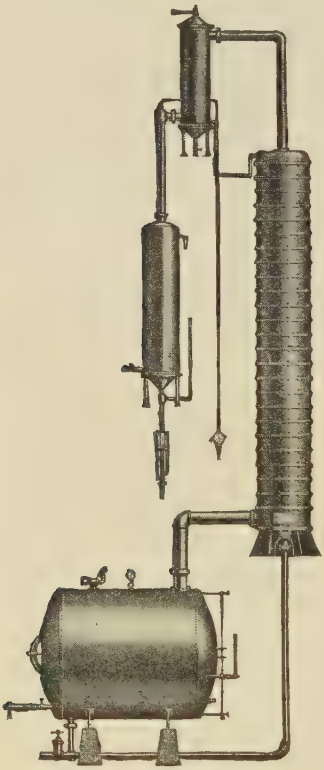

Fig. 41.

Lummus Refining Still. Fig. 41 shows a refining still with external reflux such as is used in refining benzol and toluol and concentrating aqueous solutions of alcohol, acetone, etc. The still is heated by a steam coil, which may be perforated for direct steam distillation. The vapors pass though the column which is made up of a number of sections flanged or bolted together. Each section is provided with a separate deck or dephlegmator and equipped with vaporizing hoods. The refluxing is done in the tubular reflux, the condensed portion being returned to the column through the return pipe, which is shaped so as to form a seal against the vapors in the column. The vapors which are not condensed in the reflux then pass on into the final condenser. Other parts of the apparatus are the pressure and vacuum safety valve; the temperature recorder for the vapors passing into the final condenser; the product gauge for testing the final product and observing the rate of flow; the return pipe by which the liquors may be returned to the still or drawn off.

Hodges Two-effect Water Still. For many industrial operations it is absolutely necessary that a pure water be available. This has led to the building of stills that will produce the largest distillation at the minimum cost. In the type of still shown in Fig. 42 each cell of the apparatus is constructed of two cylindrical shells, one placed within the other, the inner shell being called the condenser and the outer the jacket. The condensers

are of heavy copper, block tin-lined, provided with tinned-copper tubes. The distillate piping is made of brass with heavy brass fittings. The

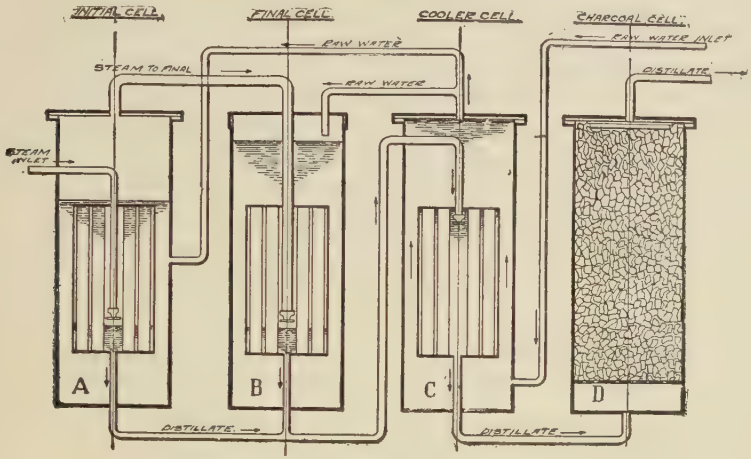

Fig. 42.

jackets are of galvanized steel, liberally proportioned. The whole is compactly assembled, occupies a minimum space, and requires the very sim-

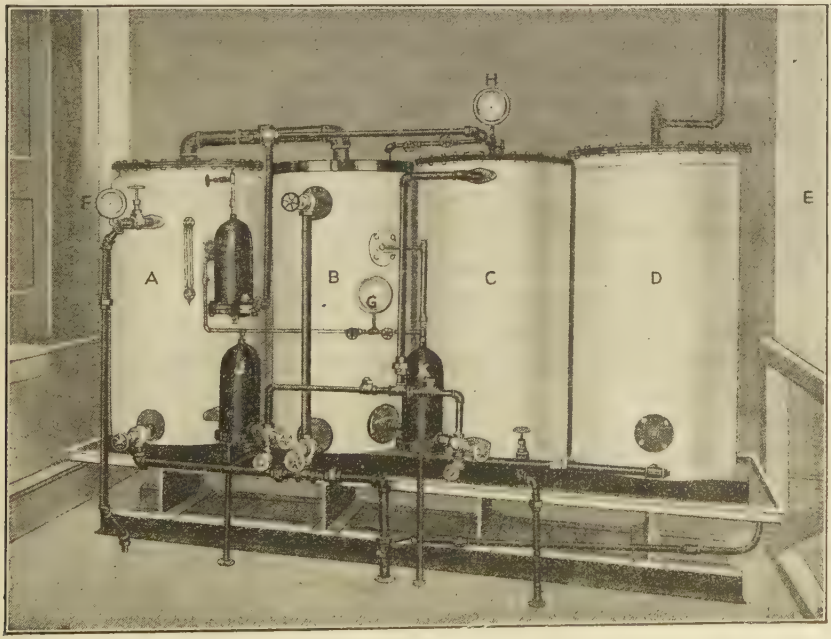

Fig. 43.

plest foundation. The initial cell of these two-effect stills is heavily insulated to conserve the heat of the steam being condensed in the first con-

denser. This materially increases the operating efficiency of these stills, and is a secondary reason for their economy.

Live steam enters the condenser of the initial cell (*A*) at a pressure of 10–25 pounds, varying with the capacity of the still, and is there condensed, the distillate flowing into the distilled water header. This steam, in condensing, evaporates the surrounding jacket water into steam of a lower pressure, which passes into the condenser of the second effect (*B*) where it in turn is condensed, flowing as distillate into the distilled water header as in the first cell. This water then flows through the cooler cell (*C*) where it gives up its heat to the entering cold raw water, and out at the bottom into the charcoal cell (*D*). After passing upward through granulated charcoal, the distillate is ready for use. The raw water enters the bottom of the cooler cell (*C*) and passes out at the top, being raised in temperature to about 160°, and is then used to supply the initial and final jackets. With this process no aeration is necessary, as all obnoxious and corroding gases are automatically eliminated from the distillate. Fig. 43 shows an actual photograph of the still set up and ready for work.

Conveying Solids. Although the man with a wheelbarrow is the simplest method of conveying solids, he is at the same time the least economical. A steel tray wheelbarrow weighs from 60 to 70 pounds and will hold about 2 cubic feet. In a general way the laborer pushes the barrow through 200 feet in a minute and consumes about $1\frac{1}{2}$ minutes for loading and unloading. Larger barrows are made with two wheels, weighing from 200 to 250 pounds and having a capacity of 8 to 9 cubic feet. As a rule barrows are used on level surfaces only, and are made of various shapes to adapt them for special purposes. In some cases it is advisable to lay steel tracks and draw the cars by means of electric motors or small locomotives. The arrangements for dumping the cars vary to some extent, but of those in common use may be mentioned the V-shaped dump car, the gabled or saddle-bottom dump car, and the hinged-end dump car.

Cars which have to go up a steep incline may be hauled by a wire cable or run into an elevator. Endless chains or cables provided with catches to hold the car while it is being drawn up the incline are especially adapted to mining operations. An aerial cableway is often used where the country is rough and where it is necessary to cross a stream. The cable of wire or rope is suspended from towers and is usually endless. Along it are run carriages to which skips or buckets are attached. Material may also be moved by the use of the revolving locomotive crane with clamshell-bucket or other form of container. A very efficient form of transportation is by means of the belt conveyor. These belts are usually made of rubber or cotton. The rubber belts (cotton duck coated with rubber) are especially designed for rough usage, whereas the cotton belts are better fitted for the carrying of boxes and packages. The belts, which may be flat or troughed, are run on rollers for support, the motion being imparted by a head pulley, and the slack taken up by the foot pulley. Different types

of rollers are used according as the belt is flat or trough shaped. The capacity of such a conveyor depends upon the width of the belt and its speed, a troughed belt being able to carry two or three times as much load as a flat one.

Hot or very rough material is generally transported in bucket conveyors carried on rollers and joined together by a roller chain. Apron conveyors are made by attaching light strips of wood or metal to link chains, thus forming a continuous belt much used for handling light packages.

In drag or flight conveyors the material is pushed along, the simplest form being one in which the plain scraper is drawn by a central rope or wire. In the suspended draw conveyor the flights are attached to cross-bars having wearing shoes at either end which slide on angle-iron tracks. In the roller flight conveyor the shoes are replaced by rollers.

The screw conveyor consists of a shaft around which metal flights are bolted to form an endless screw. This shaft, rotating in a trough, pushes the material along.

When material is to be lifted any distance it is done by bucket elevators. The buckets are fastened to belting or link chains. A bucket shaped like the letter L is easily discharged, and is, therefore, largely used for conveying pasty material; those shaped like the letter V have a larger capacity, but do not empty so readily as the L-shaped. The buckets may be made of steel, malleable iron, or copper, according to their use. They are also sometimes perforated to allow the material to drain, while others have saw edges, like those used for lifting tanbark and such material. The belt to which the buckets are attached passes over two pulleys, and the material is discharged by centrifugal force as it goes over the top one. For conveying barrels and boxes special elevators have been designed.

Conveying Liquids. The simplest problem which presents itself is the conveying of a liquid from a higher to a lower level, in this case gravity is the motive force; that is, the liquid is made to flow by means of a *head.* Liquids are usually conveyed in pipes which may be made of a variety of materials. For water, galvanized or cast iron, lead, copper, tin, and alloys, also ebonite, are used; for waste material, earthenware and cement pipe. Glazed pipe or vitrified tile find application for acid liquids; they are rather fragile, however, and should not be exposed to over 20 pounds pressure to the square inch. Wooden pipes, which are made of staves bound together with steel bands, are much used for beer, vinegar, organic acids, and dilute mineral acids. Lead pipe is very valuable in chemical industry, as it resists corrosion, but is not satisfactory when exposed to heat or pressure. For this reason iron pipes which are lead-lined are better. Tin pipes are sometimes used in breweries, and for conveying distilled water, carbonated water, vinegar, and wine; but tin-lined copper or iron pipes are less expensive. Copper and brass pipes find extensive application, expecially in the manufacture of dye-wood extracts and tanning materials. Wrought iron, either plain or galvanized, is adapted

to the distribution of water, while cast-iron pipes are employed for conveying concentrated acids.

Elevating Liquids. The most common method of lifting liquids is by pumps, which may be driven by steam, electricity, water, belt, or gear. The pressure secured in a plunger pump is due to the force of a piston, whereas in a centrifugal pump the pressure is obtained through a rotary motion imparted by means of revolving fans. The pulsometer and hydraulic ram are used to a limited extent.

To withstand the action of acid and alkaline solutions, pumps are made of various materials, but for the elevation of more corrosive liquids the acid egg is generally used. Acid eggs are usually made of acid-proof cast iron, heavy enough to withstand the necessary pressure; they are also sometimes made of earthenware. To operate, it is filled with the liquid and the ingress closed. Then, by the admission of compressed air, the liquid is forced through a tube. The Harris system of elevating liquids by compressed air consists of two cylinders, opening into common fill and discharge pipes, the cylinders being filled by suction and discharged by pressure.

Where a liquid is to be transferred from a higher to a lower level the siphon is the simplest and most economical appliance. The simplest way to start the flow is to fill both limbs with the solution and plunge the short arm into the liquid contained in the upper vessel. A very convenient form of siphon can also be arranged by having a swivel pipe attached to the bottom of the tank, and lowering it to the proper level by means of a chain.

Liquids are sometimes raised or conveyed by injectors operated by steam, their efficiency depending upon the principle of the difference in velocity of a jet of steam, issuing from an orifice, and that of a jet of water. The solutions raised by an injector become heated and diluted by the condensed steam.

Conveying Gases. Gases, whether of value for manufacturing purposes or of no special value, have to be conveyed from one part of the plant to another, or entirely removed, as the case may be. For this purpose are used pipes of sheet iron, galvanized iron, cast iron, or wrought iron, as well as flues of brick, concrete, and lead-lined wood. Gas blowers and exhausters are made either to overcome a low counter-pressure or rarefaction such as occurs in ventilation or to overcome high counter-pressure, or exhaust against a high rarefaction. These go under the name of compressors and exhausters. Fan blowers consist of a number of blades fixed on a rapidly revolving shaft. They are used only where the counter-pressure is very slight. In pressure blowers the blade widths are parallel with the shaft and enclosed in a casing, usually of metal. The higher the speed at which the blades revolve the greater the pressure.

Chimneys are often used to carry off noxious gases as well as to create

a draft and promote combustion of fuel. For a good draft height is especially desirable, while for the removal of noxious gases, size is perhaps the most important. Forced draft may be produced by blowing air through the flues or by exhausting the gases formed during combustion. That chimneys deliver noxious gases at a sufficient height to prevent deleterious action on vegetable and animal life should also be taken into consideration.

Refrigeration. The principle involved in all refrigerating machines is the absorption of heat by the evaporation of a volatile liquid. Among the substances used are liquefied ammonia, sulphur dioxide, and carbon dioxide, ammonia being the most common both in the *compression* and the *absorption* systems.

Compression System. The gas is heavily compressed and liquefied by passing it through coils over which cold water flows; the liquid is then passed through a small opening into a large coil of pipe. The expansion of the ammonia from a liquid to a gaseous state causes the absorption of much heat with the result that the temperature falls below the freezing-point of water. The gases formed in the expansion pipes are rapidly exhausted by means of a pump and returned to the compressor, where the cycle is repeated, it being necessary to supply only sufficient ammonia to replace that lost by leakage.

For the manufacture of artificial ice the expansion coils are surrounded with a strong brine or calcium-chloride solution, in which galvanized iron boxes filled with water are immersed. When used for cold storage it is desirable to increase the cooling surface of the expansion coils. The pipes are suspended from the ceiling of the room, and cast-iron disks are placed at frequent intervals on each pipe perpendicular to its line of direction.

Absorption System. The Absorption Refrigerating Machine consists of a generator, analyzer, dehydrator, ammonia condenser, ammonia receiver, exchanger, weak aqua cooler, absorber, strong aqua tank, aqua ammonia pump, and pressure gauges. In operating this machine, steam admitted to the generator coils heats the aqua ammonia to boiling. The liberated gas passes upward through the analyzer, mounted on top of the generator, where some of the water still left suspended in the gas is removed by coming in direct contact with the incoming strong aqua ammonia from the absorber. On leaving the analyzer the gas enters the top of the dehydrator, where the remaining water is condensed. The now anhydrous gas enters the ammonia condenser, where it is liquefied, and is then drawn into the anhydrous liquid ammonia receiver. From this receiver it goes to the evaporating coils in which the refrigerating effect is produced. The expanded gas from the evaporating coils then enters the absorber, where it comes in contact with weak aqua ammonia, thus producing a solution of strong aqua ammonia. The strong aqua ammonia overflows from the absorber into a strong aqua tank; the aqua ammonia pump, taking its suction from this tank, discharges the strong aqua am-

monia into the exchanger at the bottom of the shell. In passing through the exchanger the liquid becomes heated to within 35° to 40° F. of the temperature of the generator by the weak aqua ammonia from the generator. On leaving the exchanger the strong aqua ammonia enters the top of the analyzer, where it is still further heated by passing over the baffle plates and coming in direct contact with the liberated gas from the generator. From the analyzer it enters the generator at very near the temperature due to the steam coils of the generator, is again boiled, and the cycle repeated.

Chemical Apparatus. Owing to the recent development in the country of the manufacture of dyestuffs and intermediates, it has likewise become necessary for the machinery maker to develop apparatus for this purpose. A description of some of the most important forms is given below.

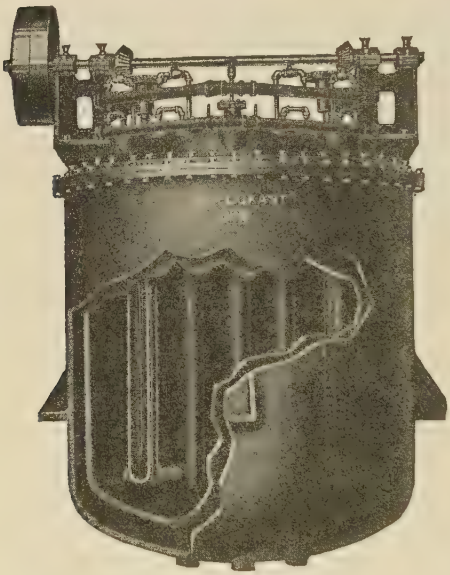

FIG. 44.

Nitrators. Many types of kettles for the nitration of aromatic hydrocarbons have recently been placed on the market. One of them, shown in Fig. 44, consists of a special cast-iron body surrounded on the sides and bottom with a cooling jacket. The large size also contains a series of closed end tubes, providing quick cooling facilities in the center as well as along the sides of the interior. Water is forced to the bottom of the tubes which are individually controlled. The temperature of the overflow from each tube can be noted and is regulated by a valve. The use of these tubes is made possible by casting the tubes without chaplets, thus insuring freedom from leaks. The apparatus is constructed throughout to withstand the heavy duty it is designed to perform. Three "boat type" propellers combined with the "bumped" bottom of the nitrator insure thorough agitation of the liquid, especially in the center. Other features are ball bearings and special semi-steel cut gears. In the smaller sizes the tubes are omitted, as sufficient cooling facilities are contained in the outer jacket.

Reducers. In order to convert nitro-compounds into amino bodies, special forms of apparatus have been devised. Fig. 45 is particularly noted for its large output and ease and cleanliness of operation. Carefully constructed to meet the working conditions for which it is

designed, the apparatus consists of a specially constructed cast-iron body.

The bottom and lower portion of the sides are lined with special quality liner plates, which are readily removable and can be renewed as occasion requires. The side plates are reversible, so that the upper portion of the plate can be used when the bottom part has become worn. The shaft and agitator are suspended from a bearing in the top of the reducer and are further supported by a heavy bearing in the yoke midway in the reducer, as illustrated, thus eliminating the objectionable bottom or step bearing commonly used. A special feature of both shaft and agitator is that they are hollow, the steam being introduced through the shaft at the top and distributed in the reducer by means of outlets in the agitator. The agitator is of the tooth type, which insures better agitation and requires less power to operate than the plow type sc commonly used.

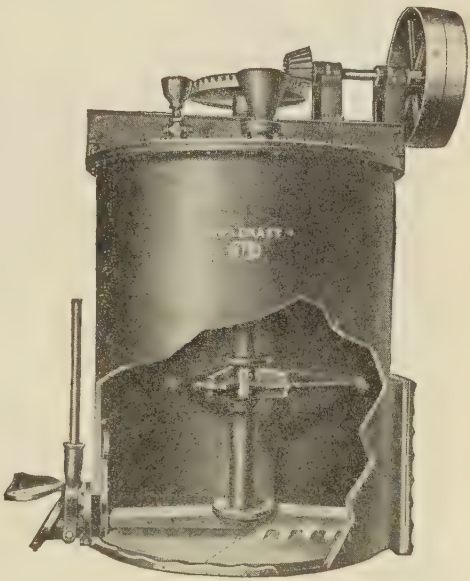

FIG. 45.

A large door on the side facilitates the removal and renewal of the liner plates when required, this door being fully protected by the lining. Another feature is the improved unloading device which automatically raises the valve when opened and wedges it in position when closed.

Sulphonators. Many oils as well as other organic products must be treated with concentrated sulphuric acid. This is done in a sulphonating apparatus, Fig. 46. As will be seen, the design of the sulphonator is especially heavy and durable. On account of the action of the acids commonly treated, a special quality of metal is used in the construction of the apparatus. The sides and bottom are steam jacketed. Efficient agitation is provided by means of "boat type" propellers attached to a shaft which extends through a stuffing box in the cover, operated by means of special semi-steel cut gears. Lugs for supporting the apparatus are provided.

Autoclaves. Many organic preparations require that the reacting bodies be subjected to elevated temperatures and under a certain amount of pressure. The illustration, Fig. 47, shows a type of this form. Autoclaves are built for any pressure desired and are constructed of cast steel,

bronze, or cast iron, depending on the pressure desired and the nature of the material to be treated. They are also built with or without outer jacket and with or without stirring devices. Where the action of the material being treated makes it desirable, a special lining of acid-resistant or other metal is provided.

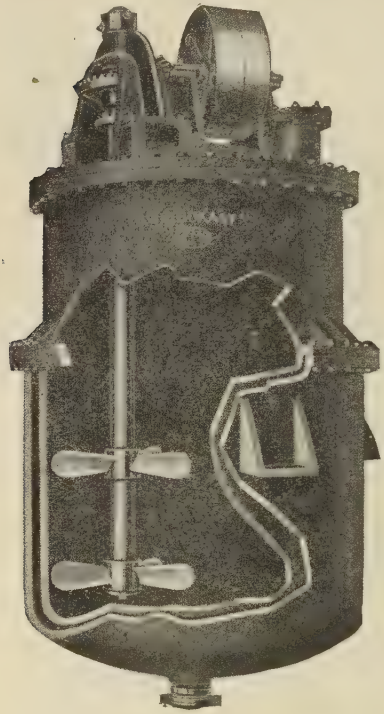

Fig. 46.

Hydraulic Presses. Hydraulic pressure as a mechanical principle has been known and understood for centuries, but its development as an industrial factor and its application to modern processes are of comparatively recent origin. For scarcely half a hundred years has its use been a commercial fact. During that time, however, the attention of chemical manufacturers has been directed towards its possibilities. The principle of hydrostatics depends upon the fact that pressure applied to any area of confined fluid is transmitted to every other equal area either of the fluid or the walls of the containing chamber without diminution. In its application every simple machine produces speed at the expense of power or the reverse. Through the medium of the hydraulic pump and press, hydrostatics convert a small, rapidly moving force at the pump plunger into a large, slowly moving force at the press ram and with no perceptible loss by friction. A machine operated by this principle is more nearly automatic in action and is more easily controlled than any other. The pressure on the press ram exceeds that applied to the pump plunger as many times as the area of the ram end is greater than that of the pump plunger head. Thus, by this form of pressure a small pump drives water or other liquid into a reservoir under pressure. The pressure so

Fig. 47.

developed exerts its influence upon a piston which in its turn transmits it to the material under treatment. Several forms of presses are illustrated below and in each case a note is given as to their particular use.

Hydraulic Abrasive Wheel Presses. Fig. 48 illustrates a heavy design of hydraulic abrasive wheel press. This type of abrasive wheel press is

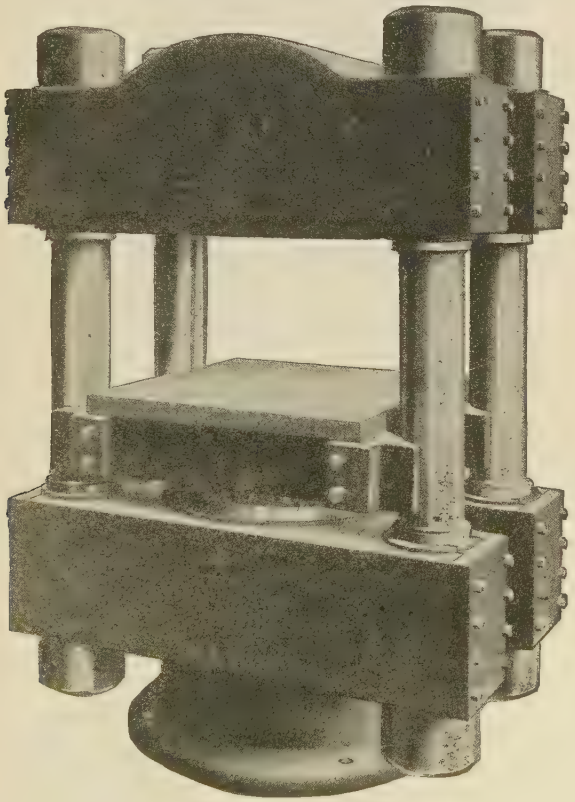

Fig. 48.

used in forming wheels of emery, corundum, carborundum, alundum, crystolon, aloxite, carbolite, and carbondite.

Hydraulic Chamois Skin Press. This press, Fig. 49, is used for "degreasing" purposes in the manufacture of chamois skins. The equipment includes two curbs mounted on trucks in which the skins are pressed. The curbs are made of wood staves reinforced with iron bands. The skins do not come in contact with anything but wood. The curbs are made in three sections, one being stationary and securely fastened to the truck, the other two sections being hinged to the stationary section and provided with substantial locks. A slightly raised section in the floor

of the truck fits the interior of the curb. The trucks are fitted with stops which center each truck in the press. They are also fitted with nipples

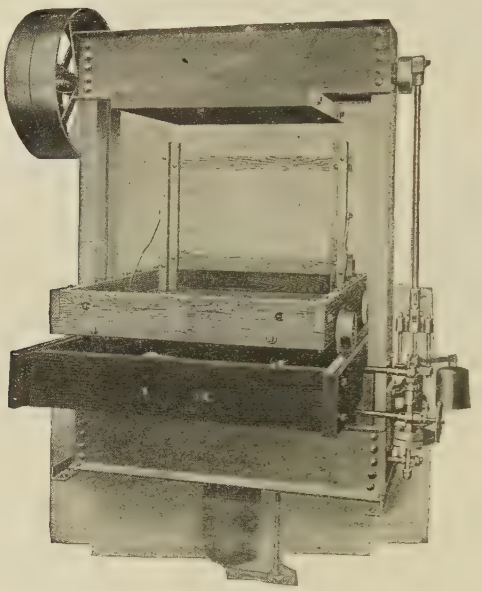

FIG. 49.

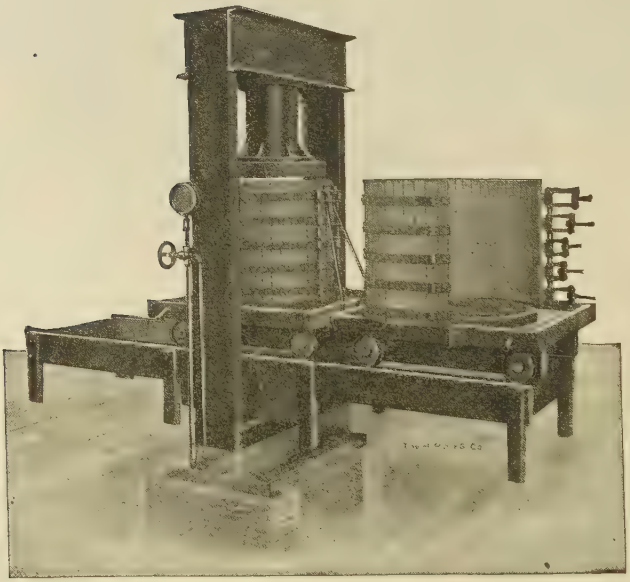

FIG. 50.

to which hose can be attached and through these the liquid pressed from the skins is drawn off.

Hydraulic Tankage Presses. This illustration, Fig. 50, shows a tankage press for small requirements. These presses are used largely by

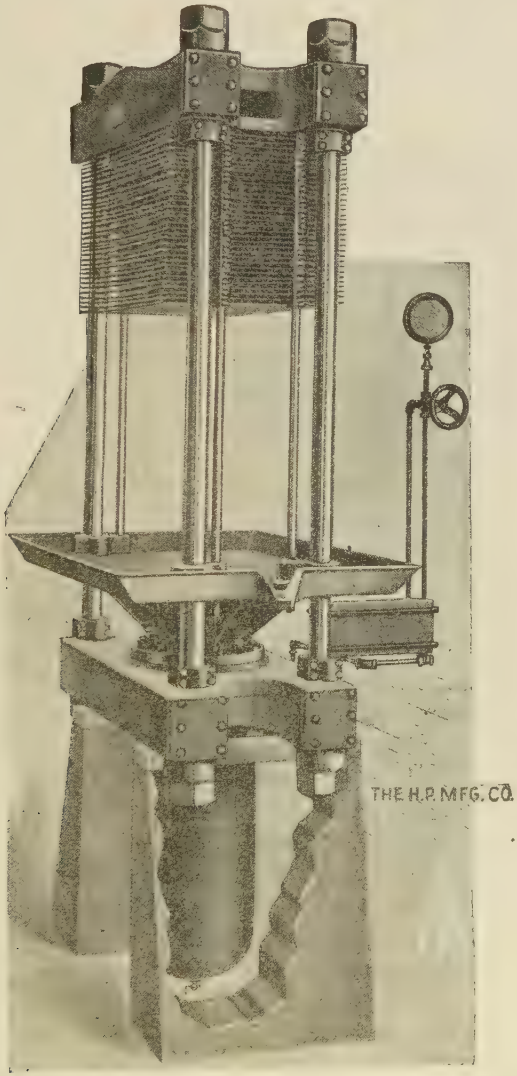

Fig. 51.

butchers for expressing grease and moisture from tankage. This design of press is equipped with the power attachment and one pump mounted on the press.

The illustration also shows the press erected on a floor, which, if substantial, forms a suitable foundation. A hole is cut through the floor

to receive the cylinder and pipe connection. This is the proper way to erect such presses if extended tracks are to be built on one or both sides of the press.

Hydraulic Oleo or Cold Presses. This type of oleo press, Fig. 51, used for the cold pressing of tallow stock, is equipped with pin bars and pins for holding the plates in the upper part of the press after the pressure has been applied. After the pressure saucer has been lowered by the return of the press ram, the plates are lowered and unloaded and reloaded one at a time. This obviates the necessity of removing the plates from the press. Black or galvanized steel plates are used between the layers of material to be pressed. Camel's hair cloths are used for wrapping the cakes while being pressed.

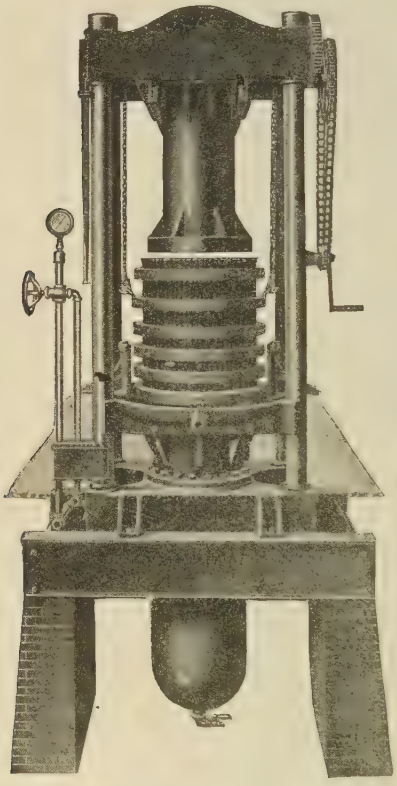

Fig. 52.

Heavy Pressure Hydraulic Curb Presses. The curb press illustrated by Fig. 52 is a popular design among the largest meat packers and renderers in the world. The press is used largely for pressing lard, grease, or tallow from packers' and renderers' scraps. This design represents the very best that mechanical skill can produce. The construction is entirely of steel, thus assuring the greatest factor of strength for the heavy pressure the press is capable of exerting. The overhead plunger and the saucer are usually steam heated. Division plates are furnished to divide the cheese into layer form for efficiency in pressing and drainage and for convenience in handling solids after being pressed.

The cheese is ejected from the curb by hydraulic pressure in the following manner: After the pressing operation is completed, the chains are hooked on to the curb and the slack is taken up by the windlass attachment. Before attaching the chains, the pressure is released just enough to prevent any strain on the chains other than holding the curb in an elevated position. After the chains are attached, the operating valve

is opened, which permits the saucer to return to its lowest position. The curb-lifting brackets are then pushed into position underneath the lower curb band and the pressure is applied, which causes the overhead plunger to force the pressed cake into the saucer below. The saucer is then lowered, brackets are removed, and the curb is lowered to position in the saucer by means of the windlass attachment.

Double Hydraulic Seed Oil Press. The machine illustrated by Fig. 53 is a double hydraulic press used for extracting oil from various oily seeds. This type of press is primarily designed for the first pressing of seeds. The presses are equipped with two solid steel slat curbs which retain the crushed seeds for receiving the pressure. However, this type of press is often used for the second and later pressings, as well as the first pressing.

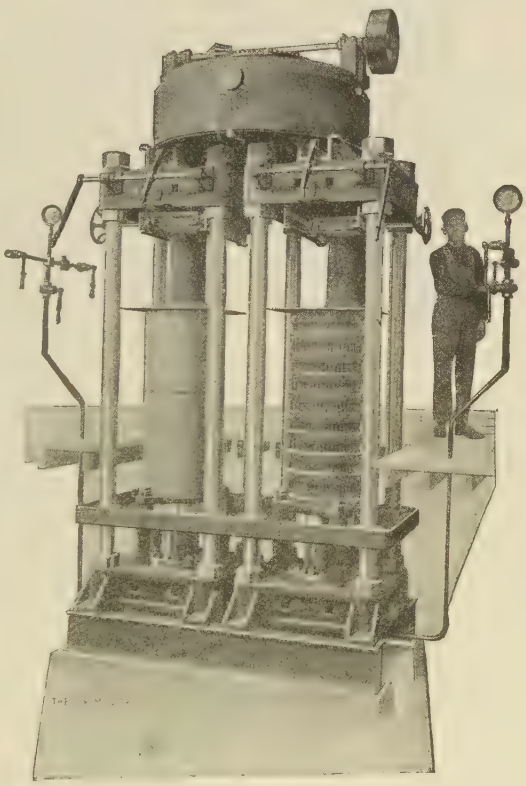

FIG. 53.

Prior to pressing, the seeds are reduced to a crushed condition by means of crushing rolls. The crushed seeds are then elevated to the cooker mounted upon the top of the presses. The cooker is filled with the crushed seeds and thoroughly agitated, heated, and damped, if necessary. In the bottom of the cooker are two openings which correspond to two chambers in the head of each press. These chambers are opened and closed at the top and bottom by slides operated by levers. The press chambers hold just enough material for composing one cake, which is placed in the retaining curb and a perforated division plate is laid on its top. This operation is repeated until the entire press is charged.

Prior to filling the retaining curbs, the plungers which project into them are rolled back and out of the way. One of the presses in the illustration shows the overhead plunger rolled back and the curb ready to receive the

crushed material; the other press shows the plunger in position to receive the pressure. During the pressing operation, metal shields are placed around the retaining curbs for the purpose of conducting the oil to the pan below.

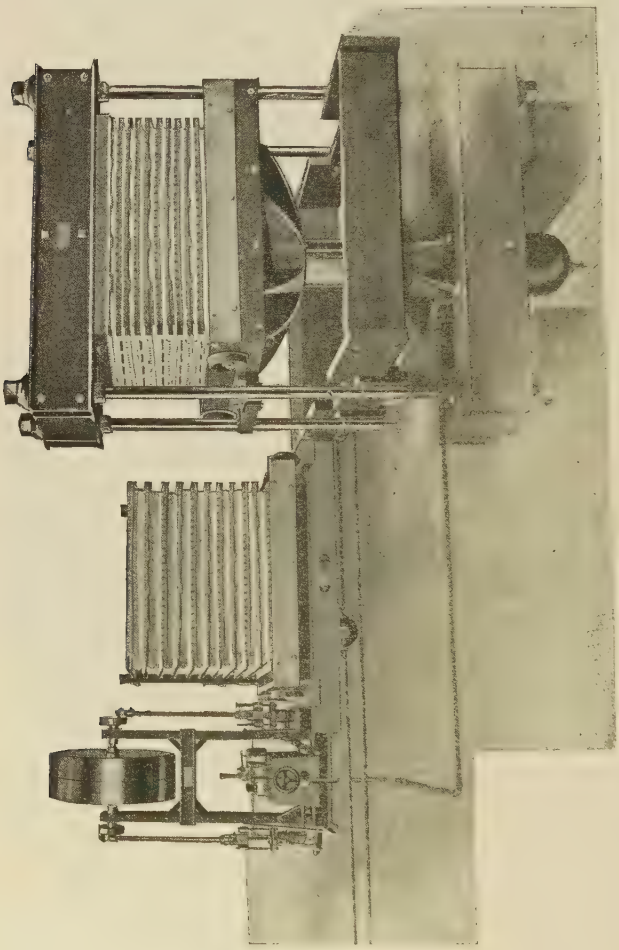

Fig. 54.

After pressing, the cakes are removed from the retaining curbs by rolling back the overhead plungers and applying the pressure. The curbs being bolted in a stationary position to the press pan (saucer), the press rams work up through the curbs and force the pressed cakes out at the top, whence they are removed by the press operator. When filling the curbs, most operators run the ram up into the curb and then permit it to recede as the material is drawn from the chamber above. This makes it more convenient for spreading the material and placing the division plates.

The material, after being pressed on this type of press, usually is again reduced to a meal by a grinding machine and formed into cakes, then repressed in a box or plate type of press. In some instances, however, the material is again pressed in the curb retaining type of press as here described.

Hydraulic Cider, Wine, and Grape-juice Presses. In every section of the world where apples and grapes are extensively grown, the cider, vinegar, wine, and grape-juice industry is a very important one and is each year becoming more so because of the growing tendency to conserve all waste in fruits, especially apples and grapes. Hydraulic presses for this industry are of steel construction throughout, except for such parts as come in direct contact with the juice. Hard wood is used here because metal will injure the juice. In connection with presses used in this industry, graters and crushers are used, to thoroughly break up the juice cells and reduce the fruit to a fine pomace, which is then built up by means of racks and cloths into a cheese for pressing. The rack and cloth system of pressing is the most approved and modern retaining method in use to-day, because it provides easy means for obtaining the maximum amount of juice from the fruit with the least effort on the part of the operator as well as the press. The racks furnish easy drainage for the juice from the center of the cheese. Cider and grape-juice presses are built in many styles to suit varying conditions. The most common type is the combination design which is a complete unit machine. This type affords means of performing all operations at the press, including elevating, grinding, crushing, and pressing. Where it is more convenient to have the fruit ground or crushed by a grater or crusher installed separate from the press, an independent press with the transfer car system is preferred. Fig. 54 illustrates this type of press. The double-transfer car system is shown but the single-transfer car system may be used just as conveniently, in which case a track is provided on both sides of the press, on which single transfer cars, carrying stock trucks, are run between the grinding or crushing point and the press.

CHAPTER II

WATER FOR INDUSTRIAL USE

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Choice of Industrial Water Supply. The quality of water supplies for municipalities has attained a prominent place in technical literature, for man's first requirement of water is that it shall be fit to drink. The advantages of removing color, odor, taste, turbidity, and harmful bacteria are so well known by the public that purification of this character is insisted upon and is classed among the fundamentals of water-supply engineering. The literature of water for industrial use, however, is meager. The effect upon many industrial processes of the substances present in water is largely a matter of conjecture, though the advantages of treatment to secure water of better quality for some processes is well known. Nevertheless, each water-using industry depends in a notable degree on the quality of its water supply for its financial success or the quality of its product.

Quality of water may be so important as to be the controlling factor in the location of an industry. Knowledge of character of available water supplies over large areas, as well as knowledge of effects of impurities of water on industrial processes, is essential to a wise choice of location. The many water analyses published by the U. S. Geological Survey and by State and Municipal bureaus, primarily for the benefit of prospective water users, and the analytical data on file in the offices of railroads and other large industrial users of water are helpful in making such a choice. If the location of the industry is fixed by other considerations, it is necessary to obtain data on supplies available in the locality in order that the source of water best suited to the industry may be selected for use. Generally, if a municipal water supply is available it should be chosen, for such a supply is as a rule cheap, plentiful, and of as good quality as any to be had. Too often quantity or cost is considered to the practical exclusion of quality of water. The choice between stream waters and ground waters must often be made. Stream waters are usually the lower in dissolved mineral content but vary greatly with change of stage in quantity, turbidity, and concentration, and even in chemical character. Ground waters are likely to contain deleterious gases, relatively high concentration of mineral constituents, high content of heavy metals, and are the more extreme in chemical type. Ground waters are normally the more concentrated

the deeper the horizon from which they are drawn. Quantity is likely to decrease, and of necessity the cost of pumping increases with depth to water. Generally, therefore, and this is particularly true in regions of igneous rocks, the ground water nearest the surface affords the best industrial water supply. This rule is by no means universally applicable in regions of sedimentary rocks and in such regions endeavor should be made to tap a known aquifer that experience has shown to afford the best water supply.

Once the location of the industry and the source of water have been determined the chemist at the works must solve the problem of making the best of the water supply to be used. It is possible to produce water of any desired quality from any water supply whatever. The problem is one of adjustment of cost of treatment to value of benefits derived. Obviously, the purification process that will give a maximum excess of value over cost of treatment is the one to be selected.

Source of Impurities in Water. The industrial value of water is due in large measure to its property of dissolving in greater or less degree nearly everything with which it comes in contact. Because of this property, however, pure water is unknown in nature. Even rain, the purest of natural waters, is contaminated by finely powdered mineral matter, particles of plants, ammonia, carbon dioxide, oxygen, nitrogen, and other substances gathered in its fall through the atmosphere. On reaching the earth, rain flows into streams as surface run-off, passes into the air as vapor, or sinks into the ground, a storage reservoir from which it eventually emerges as vapor or surface water. Surface water is the chief contributor of turbidity to streams, while to the ground water is chargeable a major part of the dissolved mineral impurities. Whether passing over the surface or slowly percolating underground, water takes into solution a part of the materials with which it comes in contact. Impurities derived from the air assist in the solution of rock-forming minerals, while all the dissolved materials exert an influence one upon another. The chemical constitution and physical condition of an area is therefore reflected by the water it furnishes.

Most wells and springs indicate the nature of a very local geologic area, while running streams reveal the local conditions of their drainage areas and thus provide an approximate average index of the geology of a much larger territory. If water analyses are not available geologic data may assist materially in postulating the character of a water. The older crystalline rocks afford waters of low concentration free from permanent hardness, though temporary hardness and relatively high content of silica may be expected. These are among the best waters for use in boilers, for processes of the textile industries, for paper making, and in fact for most industrial processes. Such waters are prevalent in the upper Mississippi River basin, in the region from the Appalachian Mountains to the Atlantic coast, from New England to the Gulf of Mexico, and in rela-

tively small areas in various sections of the United States. Waters from basalts and rhyolites, such as are found in many parts of the Rocky Mountain and Pacific Coast States, are likewise to be commended for industrial use, though these are likely to be somewhat more concentrated and may carry sulphate. Sedimentary rocks, particularly marine sediments, such as are found throughout the greater part of the Mississippi Valley, carry waters of still greater concentration. Waters from limestones are very hard and those from magnesian limestones and dolomites are among the worst boiler waters, causing both scale and corrosion. Sandstones differ greatly in content of soluble constituents and in quality of waters, and this is true also of shales. The best and the worst of industrial waters may come from shales of widely differing character. Many sandstones and shales afford waters of high permanent hardness. These rocks, like the limestones, cover great areas, and once the character of the water from any particular stratum is determined, the general characteristics of a water from the same stratum many miles distant can be forecast with a fair degree of certainty.

Amount and intensity of rainfall, assisted by surface slope and permeability of soil, play an important role in quality of water. Other things being equal, least mineral matter is found in waters from regions of highest rainfall. In periods of drought ground water is the chief source of stream flow and in consequence the stream waters are then most highly mineralized. At such times the ground water is drawn upon for the support of vegetation and its mineral impurities are thus concentrated. A gentle rain will dilute the ground water and cause it to feed the streams more generously but will not contribute appreciably to stream flow by means of surface run-off. A hard rain, on the contrary, may contribute comparatively little to ground water but will wash much dirt into streams, increase their loads of suspended matter, and dilute their dissolved mineral impurities. The amount and character of impurities in water, therefore, depend on numerous conditions and are derived from many different sources.

Sanitary Analysis of Water. A sanitary analysis of water ordinarily consists of physical examination for temperature, turbidity, sediment, color, and odor; microscopical examination for number and kinds of microscopic organisms; bacteriological examination for total number and number of certain kinds of bacteria; and chemical examination, usually including total residue on evaporation, loss on ignition, fixed solids, alkalinity, hardness, chlorine, iron, nitrogen as albuminoid ammonia, nitrogen as free ammonia, nitrogen as nitrites, nitrogen as nitrates, total organic nitrogen, oxygen consumed, and dissolved oxygen. Sanitary analyses in connection with field examination of possible sources of pollution are of value industrially as a guide to quality of water used in the manufacture of food products where pollution is suspected, and are particularly useful in determining the efficacy of purification processes. In general, however, it is the mineral rather than the sanitary quality that is of chief industrial importance.

Mineral Analysis of Water. A mineral analysis of such waters as are ordinarily used for industrial purposes includes four classes of water impurities: Suspended solids, colloidal matter, dissolved gases and dissolved solids.

Suspended solids include all organic or inorganic matter that can be removed by filtering. This material is complex and consists of many chemical compounds not usually determined in detail. Two determinations are often made, turbidity (Tu), the figures for which indicate the concentration of a known standard suspended matter that will obscure just as much light as the water under consideration; and suspended matter (Sm), which is the proportion by weight of the suspended solids in the water. The ratio of suspended matter to turbidity is called the coefficient of fineness. The greater the value of this coefficient, the greater will be the average weight of the suspended particles, and hence the greater will be the ease with which they can be removed.

Colloidal matter (Cm) includes for the most part silica (SiO_2), alumina (Al_2O_3), and iron oxide (Fe_2O_3), though in some waters, more especially polluted waters, a considerable amount of organic matter may be present in the colloidal state. In a mineral analysis colloidal matter is not distinguished as such, but the three principal components are determined separately as though in true solution. There is, in fact, always some doubt as to whether the oxides in colloidal state or radicles in solution are involved. The individual analysis may indicate the state of these substances; otherwise, it is a safe rule to consider their being present as colloids when that will produce the most undesirable conditions and as radicles when as such they would be most undesirable.

The dissolved gases carbon dioxide (CO_2), hydrogen sulphide (H_2S), and oxygen (O) are not often determined, because the tests to be of value must be made at the source with special apparatus. The content of gases in stream waters is necessarily small, but in ground waters great quantities of gases may be held in solution and their industrial importance may be considerable.

The dissolved solids are ordinarily regarded as forming a balanced system of chemical values. The determinations usually made are shown in the following table, which gives also the combining weights and reaction

Basic Radicles.	Combining Weights.	Reaction Coefficients	Acid Radicles.	Combining Weights.	Reaction Coefficients
Alkali:			Strong-acid:		
Sodium (Na)	23.00	0.0435	Nitrate (NO_3)	62.01	0.0161
Potassium (K)	39.10	.0256	Chloride (Cl)	35.46	.0282
			Sulphate (SO_4)	48.03	.0208
Alkaline-earth:			Weak-acid and hydroxide:		
Barium (Ba)	68.685	.0146	Sulphide (S)	16.03	.0624
Calcium (Ca)	20.035	.0499	Bisulphide (HS)	33.068	.0302
Magnesium (Mg)	12.16	.0822	Carbonate (CO_3)	30.002	.0333
			Bicarbonate (HCO_3)	61.013	.0164
Hydrogen and weak-base:			Hydroxide (OH)	17.008	.0588
Hydrogen (H)	1.008	.9921			
Aluminum (Al)	9.033	.1107			
Manganese (Mn)	27.465	.0364			
Iron (Fe), ferric	18.613	.0537			
Iron (Fe), ferrous	27.92	.0358			

coefficients of the several radicles corresponding to the atomic weights of 1917.

The alkali radicles are usually computed and reported as sodium, the separation of the other radicles of the group being omitted. Since sodium is practically always 75 per cent or more of the group and the several members have similar significance, this practice can not be seriously condemned for most industrial purposes. The reported result in parts per million is really the sum of the sodium and three-fourths of the potassium. Calcium and magnesium are the only members of the alkaline-earth group ordinarily reported, the others, where present, being found in relatively insignificant proportion. Manganese, iron, and aluminum are often determined together as oxides and so reported. Separation of these constituents is desirable. Hydrogen is reported as representing free strong acids. Acidity is sometimes reported in terms of hydrochloric acid, sulphuric acid, or calcium carbonate. Conversion to hydrogen may be made from the following factors: $H = .0276$, $HCl = .0206$, $H_2SO_4 = .0201$, $CaCO_3$. Other radicles of the weak-base group are seldom reported, being of importance chiefly in the case of badly polluted or mine waters. Chloride and sulphate radicles are reported separately, but the other strong-acid radicles, which are rarely in sufficient proportion to be of great industrial importance, are generally omitted. The weak-acid radicles are generally determined together by the "alkalinity" titration. Separation of free carbon dioxide (CO_2), half-bound carbon dioxide (HCO_3), and fully bound carbon dioxide (CO_3) is often attempted. When the other weak-acid radicles are absent, or nearly so, as is often the case, results of this kind are satisfactory, but the possibility of the presence of disturbing factors should be borne in mind.

There are a number of so-called industrial methods of analysis giving directly such qualities of water as total hardness, temporary hardness, and incrustants. These are useful approximations but they will not be given further consideration here because the complete mineral analysis gives more definitely the information afforded by such tests and also much valuable information that they cannot supply.

Expression of Results. Statement of analyses in hypothetical combinations of the radicles has had a vogue in American water-supply literature but is being gradually superseded by statement of the weight of the radicles determined, expressed as a proportion of the weight or volume of the solution analyzed. The chief value of the hypothetical combinations is to show in part the relative reacting value of radicles, but they have been computed in so many different ways that their meaning is uncertain. The end attempted can be attained to far greater advantage by reporting reacting values (product of proportional weight and reaction coefficient; or quotient of proportional weight divided by combining weight) along with the proportional weights of the radicles.

Best modern usage favors statements of the proportional weights of

constituents found by analysis in terms of milligrams of constituent per liter of water. This is essentially a statement in parts per million by weight for waters sufficiently dilute to be used for industrial purposes and is often so reported. Conversion to this from other forms that have been extensively used can be made by use of the following factors:

From parts per hundred thousand, multiply by	10.0
From grains per Imperial gallon, multiply by	14.3
From grains per U. S. gallon, multiply by	17.1
From pounds per 1000 U. S. gallons, multiply by	120.0

Quality of Water. The kind and relative abundance of the chemical constituents determine the character of a water, and the ratio of their aggregate weight to that of the water is termed its concentration. Character and concentration together fix the quality of water, and both are of industrial importance. An analytical statement in which the reacting values of the several radicles are expressed as a per cent of their sum is aptly termed the "character formula" by Palmer.[1] It is similar to the usual formula of a chemical compound, except that it is on the reacting value rather than the molecular scale. Concentration is of course eliminated in the character formula. Natural waters form a continuous character series shading gradually from one type to another. Certain points of demarcation are especially noteworthy, however, and from them different types of waters are distinguished as follows:

1. Reacting value of strong acids not greater than that of the alkalies. Waters of this type have no permanent hardness and are therefore readily and cheaply softened. Most though not all of them are of comparatively low concentration and can with reasonable assurance be expected in regions of igneous rocks.

2. Reacting value of strong acids greater than that of alkalies, but not greater than that of alkalies and alkaline earths. Waters of this type are in general derived from marine sediments. They have permanent hardness, and therefore are relatively unsuited for many industrial processes and are difficult and costly to soften. They are as a rule considerably more concentrated than waters of the preceding class.

3. Reacting value of strong acids greater than that of alkalies and alkaline earths. These are acid waters. Most of them are the result of pollution, are the drainage from mines, or are derived from regions of volcanic activity. They are likely to be impregnated with heavy metals and are in general unsuited for industrial processes. Because of their relatively rare occurrence they need be given little consideration.

The foregoing classification is extremely broad. In connection with special problems other relations, shown by the character formula, may be important and lead to further detailed classification. Relative content of sulphate or of magnesium, tendency to form soft scale or hard scale, to

[1] Palmer, Chase: The Geochemical Interpretation of Water Analyses, Bull. 479, U. S. Geological Survey.

corrode metal containers or vegetable fibers, to foam, to harden or soften foods in cooking, etc., are all matters of importance that may be deduced without difficulty from the character formula. Concentration must also be considered in estimating the extent of action to be expected in line with the several tendencies indicated by character.

The following table includes analyses of typical waters, showing reacting values and character formulas. Waters of concentration sufficiently low to be available for general industrial use were purposely selected for these typical analyses.

MILLIGRAMS PER LITER, BY WEIGHT

	Lake Superior, Sault Ste. Marie, Michigan.	Deschutes River, Moody, Oregon.	Mississippi River, New Orleans, La.	Green River, Greenriver, Wyoming.	Youghiogheny River, McKeesport, Pa.	Bumpass Hot Springs, Shasta County, California.
Na	3.2	6.7	13.	32.	8.0	16.
K		1.6			1.8	14.
Ca	13.	5.1	32.	41.	23.	8.9
Mg	3.1	1.6	8.4	13.	6.7	5.1
Fe	.06	.04	.5	.....	4.7	1.4
Al	.....	.....	.....	.....	.....	5.3
H	.....	.....	.....	.....	.5	.37
NO_3	.50	.22	2.5	.12	1.1	trace
Cl	1.1	1.2	9.7	15.	4.5	trace
SO_4	2.1	3.6	24.	81.	123.	141.
HCO_3	56.	34.	111.	140.	0.0	0.0
Total	79.1	54.1	201.1	322.1	173.3	192.1

MILLIGRAM PER LITER, BY REACTING VALUE

Na	.14	.29	.57	1.39	.35	.70
K		.04			.05	.36
Ca	.65	.25	1.60	2.04	1.15	.44
Mg	.25	.13	.69	1.07	.55	.42
Fe	.00	.00	.02	.....	.17	.05
Al	.....	.....	.....	.....	.....	.59
H	.....	.....	.....	.....	.50	.37
NO_3	.01	.00	.04	.00	.02	trace
Cl	.03	.03	.27	.42	.13	trace
SO_4	.04	.08	.50	1.69	2.56	2.93
HCO_3	.92	.56	1.82	2.29	.00	.00
Total	2.04	1.38	5.51	8.90	5.48	5.86

CHARACTER FORMULA—PER CENT OF TOTAL REACTING VALUE [1]

Na	7	20	10	15	6	12
K		3			1	6
Ca	31	18	28	23	21	8
Mg	12	9	12	12	10	7
Fe	0	0	trace	.....	3	1
Al	.....	.....	.....	.....	.....	10
H	.....	.....	.....	.....	9	6
NO_3	trace	0	1	trace	0	trace
Cl	2	2	5	5	3	trace
SO_4	2	6	9	19	47	50
HCO_3	46	42	35	26	0	0
Total	100	100	100	100	100	100

[1] Error of analytical statement compensated by computing basic radicles as per cent of twice their sum and acid radicles as per cent of twice their sum. Acid and basic radicles therefore each aggregate 50 per cent in the character formula.

Industrial Aspects of Important Constituents. Suspended matter is harmful in most industrial processes. It is visible, however, and therefore the effects are readily observed, and the degree of purification obtained by any method of treatment is easily seen. Suspended matter may be considered chemically inert, and its effects are essentially the mechanical effects of ordinary dirt. Mechanical interference with such processes as dyeing, bleaching, and scouring, and discoloration of the products of manufacture are chief effects of using turbid water. The methods used for purifying water with respect to other substances are usually effective in removing suspended matter, so that no special treatment is required except when other purification is unnecessary. City water supplies are often treated primarily to clarify them. Filtration preceded by coagulation is always effective, though filtration alone often fails to remove fine particles of clay.

Colloidal matter, like suspended matter, is chemically inactive. Alumina is too little in quantity and too innocuous to warrant treatment. Iron oxide may precipitate and leave the characteristic reddish-yellow stain. Silica, which is a relatively important constituent of soft waters of low concentration, is not particularly deleterious, though it is likely to precipitate. It slowly forms a hard porcelain-like scale on tubes of boilers operated at high pressure and may thus cause serious trouble. No special methods for the removal of silica have been developed. It is decreased, however, by filtration, water softening, and most other methods of treatment.

Dissolved carbon dioxide is present in practically all waters, being low in streams and very high in some ground waters. This substance is an aid to corrosion of well casings, pipes, boilers, etc. It is removed by heating or by treatment with caustic lime or other suitable chemical. Hydrogen sulphide, even in small quantity, is easily detected by its characteristic odor of rotten eggs. It occurs in badly polluted streams and in many ground waters, though probably a small per cent of the well waters in the United States contain it. Like carbon dioxide it is an aid to corrosion. By reason of the fact that it forms dark-colored precipitates with many chemicals it is deleterious in many industrial processes. Treatment with chemicals or by heating removes it effectively. Oxygen is in solution in practically all waters. It may be removed by heating. It is an aid to corrosion but is otherwise generally innocuous.

Sodium and potassium are constituents of nearly all rocks and are present in all natural waters. The content of sodium is increased by several systems of water treatment. Potassium rarely has more than a fourth to a third the concentration of sodium. The compounds of these alkalies are readily soluble and therefore they are relatively important constituents of all highly concentrated waters. Happily they are detrimental in but few industrial processes. Concentration in boilers leads to foaming, and dilution must be accomplished by "blowing off" the excess of concentrated water and replacing it with fresh. This of course results in material loss of

heat. Concentration of sugar waters in refining sugar tends to produce liquors high in content of alkalies. If the proportion of alkalies to sugar is great, interference with crystallization and waste of sugar by retention in the mother liquor result. Distillation is the only practical method of purifying water with respect to sodium and potassium.

Calcium and magnesium radicles are among those most widely distributed in nature. They are present in greater or less proportion in nearly all natural waters, giving to them the property commonly known as hardness. Hardness may be defined as soap-consuming power or capacity to prevent soap forming a lather in water. The use of water and soap is necessary in all washing and scouring processes. Waste of soap in overcoming hardness before a lather is formed and before action on material to be washed can begin is a material element of expense in such processes. Moreover, calcium and magnesium form insoluble curd-like compounds with soap that cling to fabrics and interfere with washing processes. When water is heated calcium tends to precipitate as the carbonate or sulphate and magnesium as the carbonate or hydrate. The tendency to precipitate on heating renders calcium and magnesium undesirable constituents of water for all industrial processes in which water is heated or is used for cooling purposes. The industrial effects are discussed in detail in connection with several industries. Removal is ordinarily accomplished by water-softening processes combined with filtration.

Hydrogen and weak-base radicles in general are undesirable constituents in industrial waters chiefly because of the accompanying tendency to corrosion. The constituents of this group have but a weak hold on the acid radicles of the system of dissolved solids and are therefore specially susceptible to reactions in which they are deposited or otherwise removed from the system and replaced by other constituents. Solution of many of their compounds is accompanied by hydrolysis and ionization in such relation as to impart an acid reaction to the solution. The deposited constituents as well as acidity are harmful in many industrial processes. This is particularly true of iron which leaves dark stains that are very difficult to remove. In paper-making, textile-manufacturing, and preparation of beverages ferruginous waters are specially undesirable. In general, water-softening processes are effective in removing constituents of this group. Aeration and filtration through artificial zeolites are important methods of removing iron and manganese.

Nitrates are seldom prominent constituents of waters and are in general derived from the oxidation of organic matter. They are oxidizing agents and on this account are deleterious in many industrial processes, though on account of their relatively small concentration they are often ignored.

Chlorides are present in practically all waters, and, since the chlorides of bases found in water are very soluble, the chloride radicle is a prominent constituent of nearly all very highly concentrated waters. Chlorides in

processes treating foodstuffs or beverages tend to give a salty taste and excessive amounts must therefore be avoided. They affect organic matter and hence interfere with tanning, malting, fermentation, and other processes dealing with organic matter. Chlorides can be effectively removed only by distillation.

Sulphates are thought to be derived chiefly from oxidation of sulphur and sulphides. They are most noteworthy in regions of sedimentary rocks and they are directly traceable to deposits from sea water. Sulphates are undesirable constituents of boiler waters but are advantageous in processes of tanning and brewing. The ordinary processes of water treatment do not remove them. Precipitation with barium carbonate is effective and distillation may be resorted to as an extreme remedy.

Carbonates and bicarbonates can be reduced in hard waters by heating or by the processes of water softening. Treatment with strong acids is effective but is only of use in connection with a few processes. Carbonates in irrigation water are sometimes corrected by the use of gypsum or land plaster. In most industrial waters the bicarbonate is the dominant acid radicle and in moderate concentration is harmful in but few processes. Other weak-acid radicles are not of great industrial importance.

Water for Steam-making. The chief industrial use of water is steam-making. The cost of softening water by the lime-soda process is a fairly reliable index to its value for this and many other industrial purposes. The cost for softening is the sum of two figures—cost for lime and cost for soda ash, the former being about one-fourth the latter. In a general way, the amount of lime required varies with the amount of least objectionable impurities, while the amount of soda ash required varies with the quantity of impurities most deleterious in character. If, therefore, the ill effects of the latter class may be assumed as four times those of the former, the relative cost of chemicals for softening waters will represent their relative objectionableness with a fair degree of accuracy.

The customary method of interpreting the value of a water for boiler use is based on its tendency to cause foaming, corrosion, and incrustation. Such interpretation is usually made from the hypothetical combination of the radicles as salts, judgment of the tendencies of these salts being made in accordance with our knowledge or theories of boiler physics. Unfortunately our knowledge is rather restricted though our theories are numerous. It follows that the interpretation cannot always be expressed in very definite terms and if so expressed is liable to error.

Foaming and Priming. Foaming and priming are probably the least understood of boiler phenomena. Priming may be defined as an ebullition so violent that water in the form of spray is carried from the boiler before its separation from the steam can take place. It is controlled by the relations of heating surface, evaporation surface, circulation, and working load, all of which are factors of the violence and rapidity of ebullition, and by such features as dash plates, water space, and steam space, all of which

affect the possibility of violently boiling water reaching the steam exits. Priming, as thus defined, is a matter of boiler design and operation.

Foaming is the formation of bubbles upon and above the surface of the water. The less easily these bubbles break the higher will the foam rise. It may become so excessive that the bubbles, or films of water inclosing steam, pass out with the steam.

Naturally priming, or a tendency to prime, is an important factor in excessive foaming. Aside from this, the difficulty with which the steam pushes through the surface film of water and separates from it is a controlling agency. With nearly pure water foaming is very slight and never sufficient to cause the loss of water with steam in a well-designed boiler. Nearly all impurities dissolved or suspended in water increase the foaming tendency, though no two substances may do so to the same degree. As steam is used from the boiler the impurities are concentrated and finally a stage is reached which will cause excessive foaming. If, therefore, the quantity of impurities and the effect of each were known, the calculation of the foaming tendency of a water would be a simple matter. Unfortunately, our knowledge of this department of boiler physics is very slight. It is practically impossible to determine the quantity of suspended matter in a boiler at any time. Suspended matter originally present in the water is largely precipitated, while additional suspended matter is derived from loosened scale and from the precipitation of impurities in solution in the feed water. Organic matter holds a similar indefinite place in connection with foaming calculations because a large but unknown proportion is precipitated. It is, however, usually present in relatively small amount in boiler waters. Although both these classes of substances are undoubtedly important, the effect of precipitated magnesium being especially noteworthy, their role in inducing foaming cannot, therefore, be calculated from an analysis of boiler feed water. For this reason and because all other dissolved substances are relatively insignificant in amount in a highly concentrated boiler water it is generally customary to attribute foaming to sodium and potassium salts. These substances are highly soluble and their relative importance in different waters is easily determined from analyses. The expression 2.7Na+2K will represent these salts generally within 5 per cent and always within 15 per cent. It will correspond very closely to the "non-incrusting solids" usually estimated from hypothetical combinations and is sufficiently accurate for practical use. Since these compounds are at best a rough approximation of the foaming tendency of a water, nothing would be gained by the use of a more cumbersome expression from which they could be more accurately estimated. The following formula may, therefore, be adopted:

[1] Foaming coefficient $f = 62\text{rNa} + 78\text{rK} = 2.7\text{Na} + 2\text{K}$.

[1] The letter "r" in connection with the symbol of a radicle signifies reacting value.

It is to be hoped that investigation may lead to a better understanding of this phenomenon and hence to a more reliable index to the foaming tendency of waters.

The steam engineer is interested more in the number of hours his boiler may be run under ordinary load without danger of foaming than in the coefficient given above. This is really a combined index of priming and foaming and may be calculated from the formula:

$$\text{Run in hours: } Rh = \frac{a}{b}\left(\frac{c}{f} - 1\right),$$

in which a = water capacity of boiler, b = hourly quantity of feed water used, f = foaming coefficient, and c is a constant which represents in parts per million the concentration of salts that will cause excessive foaming in the type of boiler under consideration.

The usual remedy for foaming is blowing off a portion of the highly impure water and replacing it with fresh feed water. If a in the foregoing formula be made to represent the amount of water blown off at any time, the expression will indicate the length of time that may with safety elapse before blowing off again.

The following approximate values have been determined for the constant c for various types of boilers and are here adapted from Christie's "Boiler waters."

Locomotive boiler	2,500 to 3,500
Stirling boiler	4,000 to 5,000
Modern water-tube boiler (such as the Babcock & Wilcox or Heine)	5,000 to 7,000
Horizontal return tubular boiler	8,000 to 10,000
Old-style two-flue boiler	17,000

From these figures it appears that the locomotive boiler is the type most likely to give trouble on account of foaming and offers, therefore, a satisfactory basis for an arbitrary classification of waters according to their foaming tendency. A non-foaming water may be defined as one that can be used in a locomotive boiler throughout one week's work without foaming; a semifoaming water as one that cannot be used so long as a week, but one that will require one complete water change to avoid foaming in a locomotive boiler not oftener than every two days; and a foaming water as one that cannot be used so long as two days in a locomotive boiler without blowing off or changing water to prevent foaming. Accepting these conditions, the following approximate classification of waters will result:

Non-foaming; f not greater than 60.
Semifoaming; f greater than 60, but not greater than 200.
Foaming; f greater than 200.

Corrosion. Corrosion of a metal will occur in the presence of water if the metal is capable of replacing any basic radicle in the chemical system which the dissolved matter in the water constitutes. The radicle thus replaced may pass from solution as a precipitate or a gas. In boiler corrosion the metal to be considered is the iron of the boiler. The radicle which it may replace in the chemical system of dissolved solids is hydrogen, which, when so replaced leaves the chemical system as hydrogen gas. It follows that the amount of hydrogen radicle in the chemical system under boiler conditions is the controlling factor of corrosion. The calculation of this factor can be made with a fair degree of accuracy. Under boiler conditions the dissolved gases are driven out with the steam. Therefore, although some of these substances are prominent aids to corrosion when confined they are omitted from consideration here.

Hydrogen radicle as determined by analysis is the first item. It may be the cause of corrosion in the cold or under boiler conditions. To this may be added, as a result of the high temperature in a boiler, three molecules of hydrogen for each molecule of aluminum, two of hydrogen for one of iron, and two of hydrogen for one of magnesium. The reactions involved may be represented by the following equations:

$$2\,Al+3H_2O=Al_2O_3+6\,H;$$

$$Fe+H_2O\ \ =FeO+2\,H;$$

$$Mg+H_2O\ \ =MgO+2\,H.$$

These reactions probably do not occur in just this way, but they express well-known results. There are other reactions that may cause an increase in the amount of hydrogen radicle. While they will not be considered in the calculations which follow, the three given below are of interest as expressing possibilities:

$$2\,Fe+3H_2O=Fe_2O_3+6\,H;$$

$$3\,Fe+4H_2O=Fe_3O_4+8\,H;$$

$$SiO_2+H_2O\ =SiO_3+2\,H.$$

In all of these equations, except the last, the hydrogen is represented as being brought into the chemical system to replace a radicle precipitated as an oxide. In the last equation hydrogen and silicate radicles are both brought into the system. In all cases, of course, the equilibrium between basic and acid radicles in the system must be maintained.

Opposed to these reactions increasing the amount of hydrogen are others tending to decrease it. Thus under boiler conditions each molecule of carbonate radicle may combine with two molecules of hydrogen and each molecule of bicarbonate radicle with one molecule of hydrogen to form water and the gas carbon dioxide. This is illustrated by the following equations:

$$H+HCO_3=H_2O+CO_2;$$

$$2\,H+CO_3=H_2O+CO_2.$$

Thus basic and acid radicles leave the chemical system together.

The carbon dioxide so formed will pass off with the steam.

The two sets of phenomena may be combined to represent the residual hydrogen likely to be replaced in the chemical system by iron from the boiler, as follows:

Coefficient of corrosion:

$$c=1.008(rH+rAl+rFe+rMg-rCO_3-rHCO_3)$$

$$=H+0.1116\,Al+0.0361\,Fe+0.0828\,Mg-0.0336\,CO_3-0.0165\,HCO_3.$$

One of the first occurrences in a boiler is the precipitation of at least a part of the carbonate and bicarbonate radicles as calcium carbonate. Such precipitate can be acted upon, the calcium being returned to the chemical system to replace the hydrogen which forms water and carbon dioxide with the carbonate radicle. The extent of such action is not well defined. In case of maximum precipitation of calcium, carbonate and bicarbonate radicles in the above formula may be reduced by 1.008 rCa or 0.0503 Ca. The foregoing considerations afford an excellent basis for the classification of waters according to their corrosive tendencies. Three classes may be distinguished as follows:

Corrosive. If c be positive, the water will certainly corrode the boiler.

Non-corrosive. If $c+0.0503$ Ca be negative, no corrosion will occur on account of the mineral constituents in the water.

Semicorrosive. If c be negative, but $c+0.0503$ Ca be positive, corrosion may or may not occur, the probability of corrosive action varying directly with the value of the expression $c+0.0503$ Ca.

Scale Formation. The formation of scale and sludge in boilers is the most common effect of the use of impure feed water. This phenomenon is the result of heating the water to a high temperature and concentrating it. The heat reduces the solubility of many of the dissolved substances to such an extent that they leave the chemical system. Concentration may gradually increase the amount of dissolved matter to saturation, after which additional concentration will cause it to pass out of solution. Suspended matter and colloidal matter are also largely deposited within the boiler.

The purest of natural waters, if used in a boiler for a great length of time without cleaning, would produce scale or sludge. As boilers are usually operated, temperatures and concentrations are permitted which result in the precipitation of practically all suspended and colloidal matter; all iron, aluminum, and magnesium; and all calcium to the full extent of its ability to combine with carbonate, bicarbonate, and sulphate radicles. The iron, aluminum, and magnesium appear in the scale as oxides (magne-

sium carbonate may be present, but is not likely to be found in quantity in scale from high-pressure boilers), while the calcium may be present as calcium carbonate or calcium sulphate (a hydrated calcium sulphate frequently occurs, but in the modern high-pressure boiler its quantity is sufficiently small to be neglected). Whether these results are caused by a series of reactions or by a single chemical change is of little moment in connection with boiler calculations. The following reactions, therefore, are presented not as formulas for the changes which actually take place, but as equations which express the known results of changes that occur within the boiler:

$$2\,Al + 3\,H_2O = Al_2O_3 + 6\,H;$$

$$Fe + H_2O = FeO + 2\,H;$$

$$Mg + H_2O = MgO + 2\,H;$$

$$Ca + CO_3 = CaCO_3;$$

$$Ca + 2\,HCO_3 = CaCO_3 + H_2O + CO_2;$$

$$Ca + SO_4 = CaSO_4;$$

$$H + HCO_3 = H_2O + CO_2;$$

$$2\,H + CO_3 = H_2O + CO_2.$$

The hydrogen in the last two equations may include not only the hydrogen radicle found by analysis, but also that developed by the first three equations. In other words, it is *c*, the coefficient of corrosion. An estimate of the amount of scale formed is necessarily rather uncertain. The first three reactions may, without great error, be assumed to be practically complete. The division of carbonate and bicarbonate radicles between calcium and hydrogen, and the division of calcium between carbonate and sulphate radicles, are not definitely known and probably vary with different conditions of boiler operation. On this account it would seem desirable to estimate maximum and minimum values for scale formed by calcium compounds, but the difference between maximum and minimum values is small in nearly every instance, and does not warrant the use of the necessarily cumbersome formulas. Calculations based upon a formula that represents a probable average scale-forming value are relatively simple, and it is believed that they are of as great practical value as the maximum and minimum formulas. In order to conform to common usage the formula is in terms of pounds of scale per 1000 gallons of water:

Scale (Sc)

$$= 0.00833\,Sm + 0.00833\,Cm + 0.3\,rFe + 0.142\,rAl + 0.168\,rMg + 0.492\,rCa$$

$$= 0.00833\,Sm + 0.00833\,Cm + 0.0107\,Fe + 0.0157\,Al + 0.0138\,Mg + 0.0246\,Ca.$$

In this formula the value of rCa used should not be in excess of $rCO_3 + rHCO_3 + rSO_4$. (Ca should not exceed $0.668\ CO_3 + 0.328\ HCO_3 + 0.417\ SO_4$).

This formula for scale shows the amount of scale and sludge likely to be deposited in a boiler operated under the usual conditions of modern practice and its value will never differ widely from the "total incrusting matter" frequently reported from an estimation of hypothetical combinations of radicles. It is of importance to know whether the matter deposited will form a hard scale. The following formula shows in pounds per 1000 gallons the probable amount of hard-scale forming material in the scale:

Hard scale (Hs)

$$= 0.00833\ SiO_2 + 0.168\ rMg + 0.567\ (rCl + rSO_4 - rNa - rK)$$

$$= 0.00833\ SiO_2 + 0.0138\ Mg + (0.016\ Cl + 0.0118\ SO_4 - 0.0246\ Na - 0.0145\ K).$$

The value used for the parenthesis of this formula must not exceed rSO_4 or rCa ($0.0118\ SO_4$ or $0.0283\ Ca$ in the second form) nor should it be less than zero. The one or the other of the limiting values should be used when the calculated value for the expression in parentheses does not fall between them.

Dividing the value of formula for hard scale by the formula for scale, a factor will be obtained which may be called the coefficient of scale hardness. This factor shows the proportion of the total scale that is likely to form a cement-like substance upon the boiler tubes and is therefore an index to the probable hardness of the scale that will be deposited. Thus:

$$\text{Coefficient of scale hardness, } h = \frac{Hs}{Sc}.$$

From the foregoing formulas waters may be classed as follows:

Soft scale: h not more than 0.25.

Medium scale: h more than 0.25, but not more than 0.5.

Hard scale: h more than 0.5.

In addition, the following classification may be used as a prefix to the preceding:

Very little: Sc not more than 1.

Little: Sc more than 1, but not more than 2.

Much: Sc more than 2, but not more than 4.

Very much: Sc more than 4.

The committee on water service of the American Railway Engineering and Maintenance of Way Association have offered a classification of waters in their raw state that may be employed for approximate purposes, but, as their report states, "it is difficult to define by analysis sharply the line between good and bad water for steam-making purposes."

APPROXIMATE CLASSIFICATION OF WATERS FOR BOILER USE

Incrusting and Corroding Constituents.[1] Pounds per Thousand Gallons.		Classification.
More than	Not more than	
.....	0.8	Good
0.8	1.7	Fair
1.7	3.7	Poor
3.7	5.7	Bad

Foaming Constituents.[2] Pounds per Thousand Gallons.		Classification.
More than	Not more than	
.....	1.2	Good
1.2	2.1	Fair
2.1	3.3	Bad
3.3	.....	Very bad

[1] Adapted from Proc. Am. Ry. Eng. and Maintenance of Way Assoc., Vol. V, 1904, p. 595.
[2] *Idem*, Vol. IX, 1908, p. 134.

The limit of 0.8 pound of incrusting and corroding constituents for the class of good waters restricts perfectly acceptable natural waters to a small number, but the choice of that figure was probably influenced by the fact that the incrustants in poorer waters can usually be reduced by proper treatment to that amount. The limits must be interpreted liberally in practice, because they are modified by the comparative hardness of the incrustation and the different extent of corrosion effected by waters of the same mineral content but of different chemical composition. Waters of the worst class may be improved by treatment in softening plants.

Water for Brewing and Distilling. Brewing is an industry which for ideal results requires a water of rather unusual character, in that, other things being equal, a water in which large amounts of calcium sulphate have been dissolved produces the highest grade product. Of course the water for brewing must conform to the rather rigid standards of a potable supply with regard to its organic and bacterial content. This is as important to the manufacturer as to the consumer. Organic matter decomposes during the malting or germination of the barley, causing defective malting or tendencies to moldiness, and may injure the proper fermentation of the wort obtained from such malting. Bacteria and microscopic plants are troublesome constituents which produce false fermentation of the wort with detrimental and variable results in the taste of the product. The same care should be exercised in washing casks and utensils in beer making as in cleansing milk cans, etc., namely, to use a water free from organic matter, bacteria, and micro-organisms; otherwise the impurities which adhere to the casks may spoil the keeping qualities of the beer.

When the wort is boiled, organic matter in the water tends to produce a darker beer than that produced with water from which the organic matter has been properly eliminated. The decomposition products, nitrites and nitrates, effect the unfavorable growth of the Renard ferment, which is a disease of beer, spoiling its keeping qualities. In the presence of these radicles the wort often assumes a reddish color and the beer has an acrid taste.

Regarding the mineral constituents there is considerable diversity of

opinion. Soft waters effect more rapid swelling of the grain but also dissolve more of the extractive matter than do hard waters. The latter during steeping cause the formation of insoluble protein-lime compounds which diminish the yield of soluble albuminoid matter, but a water high in its content of calcium and sulphate is valuable in clearing the wort. A hardness ranging from 100 to 250 parts per million seems to give satisfactory results.

A moderate amount of iron can be tolerated but the best results are obtained with no iron present for it forms an insoluble compound with the diastase which interferes with proper manufacture of beer. A greenish color due to the formation of a tannate of iron is frequently developed, while bad tastes and odors are not uncommon phenomena as a result of brewing with ferruginous waters. Calcium may or may not have a harmful effect in brewing depending on what part of the process is considered and what acid radicles and their amounts are present with the metal. A certain amount of calcium, especially when considerable sulphate is also present, is advantageous, but when carbonates are predominant the wort assumes an intense red color, the malt and hops are acted on and proper fermentation is prevented.

Beer owes its keeping qualities to a natural acidity developed in brewing, but if carbonates are present in large amount, this acidity is neutralized and the beer is liable to spoil. Phosphoric acid, an important food for the yeast, is extracted from the grain. Carbonates neutralize this acid or acid salt, precipitate it as calcium phosphate no longer available for assimilation by the growing yeast plants. Waters containing predominant amounts of calcium and sulphate radicles have the advantage over those containing like amounts of calcium and carbonate radicles that little trouble is experienced with the formation of precipitates on boiling. The former effect a better coagulation of the albuminoid bodies and the production of a beer which keeps well. Very little phosphate is precipitated and as a result nearly all is available for assimilation by the yeast. Other advantages of beer made with "gyp" waters are that the taste is better and since less hop resin is dissolved the color is paler.

Chlorides are chiefly objectionable for the reason that they inhibit the germination of the grain. They also increase the extractive matter due to a solvent action on the albumen.

A water then for brewing should contain no organic matter, the smallest number of bacteria and microscopic plants practicable, very little iron, some calcium, only a small amount of chlorides and carbonates, preferably none, but may with advantage contain considerable sulphate.

What has been said regarding water in brewing is equally true in distilling. Harmful results are, however, intensified in malting in this industry since the malt must here be rich in diastase and consequently the germ must be developed as far as possible. Organic matter may reduce the otherwise beneficial sulphates resulting in the formation of bad

tastes and odors, and false fermentation of the grain may be expected under such conditions.

Experience has demonstrated that industries requiring water of a special nature obtain better and more uniform results in their product by first treating the water to remove its impurities and then adding to the water in measured amounts the definite chemical compounds which are known to effect optimum results. Where cost is not prohibitive this is undoubtedly the best possible procedure. In brewing, as stated, the water must be hygienically pure, free from certain mineral constituents, but may contain to good advantage certain others. Depending then on the composition of the water, it should be purified by one of the standard water softeners or an iron removal plant, with a view to removing all of the deleterious constituents and later treated with the proper amounts of calcium sulphate.

Water in Paper Making. If one considers that from 10,000 to 400,000 gallons of water are used to produce only one ton of finished paper, it can readily be understood that the quality of this water, especially for the finer products, is a matter of some importance. With the coarser grades, such as brown wrapping paper, the composition of the water does not figure so prominently. In making white or light shades of paper, ferruginous waters are out of the question unless the iron is removed. Alkali precipitates ferric hydroxide, which gives the pulp a brown color. During sizing the iron also gives trouble, and rust spots in the finished paper are a common result of the use of water containing iron.

While the ordinary constituents of a water which contains permanent and temporary hardness cause little trouble in preparing the pulp, their effect in sizing is decidedly harmful. Sizing consists in precipitating, usually with alum, the resin from a solution of a resin soap. The aluminum resinate thus formed is precipitated on the fibers. The well-known reactions between lime and a soap here take place if the water is of a calcareous nature. Bicarbonic acid decomposes the resin soap forming sodium bicarbonate and, if calcium is present in appreciable amounts, calcium resinate. This compound has a more granular consistency than the corresponding aluminum compound, does not adhere to the fibers as well, and hence is entirely unsuited for sizing purposes. Alkaline waters give trouble through the formation of double salts with alum and hence incomplete or improper precipitation of the aluminum resinate. The difficulty here may be overcome of course by the previous treatment of the water with alum but unless this is a part of a purifying system to which careful attention is paid, large amounts of alum are wasted with but partial prevention of the trouble and variable results.

The universal opinion of a large number of paper manufacturers is that turbid waters or waters carrying suspended matter are injurious to the product. Such particles resist the action of bleach and cause dark specks and spots in the finished paper, particularly noticeable in white and light shades of fine writing and art papers. Vegetable coloring matter

is productive either of streaks or of a dull shade imparted to papers that should be white. Acid waters are among the most annoying offenders. They not only give trouble with the size, decompose the colors, and produce streaks in the papers, but they also attack the expensive wire screens and dryer-felt of the machine.

Iron removal becomes an important consideration in paper making, and this is accomplished at a low cost in some places by simple aeration and filtration, though complications may enter where organic matter is present. As in other industries which have to deal with the same problem, filtration through an oxidizing filter of the permutit type successfully overcomes the difficulty. Softening can also be accomplished with a different but similar artificial zeolite, and where water of zero hardness is desired this process is to be highly recommended. A number of paper mills now in operation use the lime-soda process. These softening processes save amounts of money which depend on the hardness of the raw water, the removal of calcium and magnesium effected, the volume of water used, and the increased value of the product.

Water for Dyeing and Bleaching. Involving as it does the use of such small amounts of chemicals and large amounts of water to produce delicate coloring effects, the dyeing of fabrics often presents chemical problems of considerable difficulty. The solution of these problems often hinges on the proper choice or treatment of water used in the process. A water containing large amounts of calcium is unsuitable and even ruinous for use in dyeing with aniline colors but is essential to the successful use of logwood or weld, dyed on a mordant of iron or aluminum.

In general a water for use in dyeing should be colorless, free from suspended matter and iron, with calcium and magnesium at a minimum.

Calcium and magnesium act very much alike in dyeing. Some of the effects of these constituents are as follows: Heavy tar-like precipitates form when such aniline colors as methyl violet, malachite green, magenta, and safranine are dissolved in waters high in calcium and magnesium. This tar-like precipitate sticks to the fiber and results in uneven dyeing, poor shades, and that annoying defect of "rubbing off." Magenta and safranine are peculiarly susceptible to the influence of these constituents, the effect being noticeable in changes in both color and intensity of the coloring material. Color is wasted and flat shades are produced in dyeing with Turkey red or cochineal scarlet. In dyeing with alizarin in pure water it is necessary to add calcium carbonate to cause complete saturation of the mordants, but when calcium and bicarbonate radicles are present, carbonic acid is freed, calcium carbonate is precipitated by the heat, and the bath takes a violet color due to the formation of a compound of calcium and alizarin. If the solution is boiled, the lime lake deposits as a violet powder, and the bath cannot be used. Thus it can be seen that calcium may be necessary as well as detrimental to dyeing. It should, however, be added where necessary to the baths as a definite quantity of a

compound which will not precipitate upon heating. As a rule, calcium and magnesium salts result in uneven dyeing, fading colors, spotted effects, off shades, and a waste of color.

Iron is a very objectionable impurity. Dull and flat colors are frequently caused by this constituent, especially when dyeing on a mordant. If a water contains iron in any appreciable amounts it is practically useless for dyeing or printing with alizarin or for any of the coal-tar colors that are fixed on a tannin mordant.

In bleaching, iron is a troublesome constituent. The iron is oxidized by the bleach solutions causing yellow, brown, or muddy white effects. This difficulty can be partially remedied by acid treatment, but there is then danger of injuring the fabric. Laundries have much the same difficulty with ferruginous waters.

It is evident from the above remarks that a water suitable for dyeing and bleaching should be free from suspended matter, low in its content of iron and as soft as possible. Suspended matter is, as a rule, rather easily removed by simple filtration with or without the use of a coagulant. For small installations a rapid sand filter may conveniently be used while in larger plants settling, coagulation, and subsequent filtration through pressure filters may prove economical. Iron removal may be accomplished by aeration, aeration and filtration, or both with intermediate coagulation which, by producing a voluminous flocculent precipitate, aids in carrying down the iron. As a general rule most of the above results are accomplished by the familiar procedure of softening the water by the lime-soda process. Suspended matter is either carried down with the precipitate or is removed by the filter operated as a part of the softening plant. Iron unless unusually high is not effectively removed in softening, however, and where water must be absolutely free from that constituent, aeration, or better, treatment with a manganese permutit is being used to good advantage.

Water in Tanning. Tanning is an industry in which the quality of the water plays an important part. The large volumes of water used both in the unhairing and in the tan pit make necessary the careful selection or purification of the water supply. Unhairing consists in loosening the roots of the hair by treatment of the hides with quicklime. If the water used in this process contains bicarbonates or free carbonic acid there results a precipitation of calcium carbonate in the dermic tissues. This precipitate naturally interferes with the absorption by the cells of the hide of the tannin which is intended to convert the skin into the insoluble material, leather. In the tan pits, calcium and magnesium react with the tannin to form tannates no longer available in producing the proper effect on the hides. A considerable amount of an expensive chemical is thus wasted, and, according to one authority, the secondary products formed by oxidation of these compounds imparts to the leather a reddish-brown color which lowers the market value of the finished product. One way of obviating this diffi-

culty is to treat the water with a free mineral acid, preferably sulphuric. The acid seems to aid in swelling the hides and if used at the proper concentration for a period of time not too great, no rotting of the hides takes place. Chlorides are harmful to the proper swelling operation since they do not unite with the hide and even prevent the proper action of the acids. The ideal water for this purpose is one containing large amounts of sulphates with calcium and magnesium, preferably the latter, also present. Plumping is more readily effected, the finished leather has a finer and more compact grain, and the cut surfaces are cleaner and more shiny.

Organic matter must be entirely absent from water used in tanneries since one of the prime requisites of the finished product is that it must not decay. Organic matter tends to cause decay or "leather rot"; hence its removal becomes a matter of necessity rather than choice.

Iron is objectionable in the water supply of tanneries since the same reactions which are used in making one kind of black ink take place between the iron of the water and the tannin with which the hides are treated. In both cases ferrous iron is oxidized by the air to ferric, which then reacts to form black tannate of iron. Such coloration is of course ruinous to any but black leathers.

The lime-soda process of softening is well adapted to purifying water for use in tanning, and any one of the standard makes of softeners will, if properly operated, produce a water suitable for use in this industry.

Water in Scouring Textiles. Quality of water is an important consideration in the scouring of wool. All fresh water is added in the third or final scouring tank from which the wool emerges in its finished condition. Impurities in the water that will cling to the fiber, therefore, are obviously out of place and will have the same deleterious effects in subsequent processes as imperfect scouring. Suspended matter is composed largely of such substances. The organic matter which it contains is especially undesirable. Waters polluted by sewage or organic industrial wastes and turbid waters are always purified, therefore, before use in scouring-tanks.

A second and even more important class of impurities consists of those substances which unite with soaps used in scouring to form insoluble soaps. These substances, iron, aluminum, calcium, and magnesium, destroy their equivalent values of soap for detergent purposes, thereby making necessary the use of an excessive amount of soap. In addition, the insoluble soaps stick very closely to the fiber and make efficient scouring very difficult. On this account they are much more detrimental to the process than ordinary suspended matter composed largely of fine particles of sand. Priestman (Principles of Wool Combing, Howard Priestman. George Bell & Sons, London, 1904) states that water containing 30° of hardness (428 parts per million of calcium carbonate) cannot be used for satisfactory washing and adopts 5° of hardness (71 parts per million of calcium carbonate) as the limit of "hardening" constituents for an entirely satisfactory water supply.

Whipple [1] has deduced from a series of experiments the cost of consumption of the common household soaps by waters of various degrees of hardness. Accepting Whipple's values, with soap at 5 cents a pound, the cost in cents per 1000 gallons for soap necessary to produce a lather in water is as follows:

Soap cost

$$=11+50.05\ (rFe+rAl+rCa+rMg+rH)$$

$$=11+1.79\ Fe+5.54\ Al+2.5\ Ca+4.11\ Mg+49.6\ H.$$

If it be assumed that hardness, in addition to destroying soap, will produce a cost to the process equal to the cost of soap consumption on account of the action of the insoluble soaps formed, and that suspended matter is one-fifth as injurious as the insoluble soaps, the total cost of hardness to washing and scouring processes will be more than twice that shown by the foregoing formula.

From data of the United States Census (U. S. Census of Manufactures: 1905, Textiles, Bull. 74, p. 128), it appears that the average charge for scouring wool is 1.29 cents a pound, the expenses of scouring being 0.263 cent per pound for materials and 0.183 cent per pound for miscellaneous items. The remainder of the charge is covered by interest of 5.8 per cent upon capital invested. Where the margin of profit is so small the use of impure water assumes relatively large importance. Assuming that 1500 pounds of wool are scoured by means of 1000 gallons of water, $19.35, $3.94, $2.75, and $2.19 will represent, respectively, the charge for scouring, the cost of scouring materials, miscellaneous scouring expenses, and 1 per cent upon the capital invested in scouring establishments for each 1000 gallons of water used. Obviously under such conditions, softening hard water at a cost of a few cents a thousand gallons is a procedure of high economic value for this industry.

In scouring by the two-stage process of steeping and scouring the importance of pure water is even greater, for, in addition to the effect of hardness in the scouring operation, the recovery of potash from the steep water will be rendered somewhat more expensive and the purity of the product decreased by the saline constituents of the water. In this case all mineral impurities, not merely the hardening constituents, have a deleterious effect.

In scouring by volatile solvents and subsequent washing, since no soap is used, purity of water is a minor consideration. Suspended matter, of course, is undesirable. If the wash water is utilized for the recovery of potash, all dissolved impurities will assume importance inasmuch as some will cause scale in the evaporators and all will decrease the purity of the

[1] Whipple, G. C., The Value of Pure Water. John Wiley & Sons, Inc., New York, 1907; pp. 24–28.

potash produced. Each 100 parts per million of mineral solids in the water will reduce the purity of the potash by approximately 1 per cent.

Water used for rinsing the wool after scouring may amount to as much as 100 gallons for each pound of wool scoured. This water should be free from suspended matter but otherwise requires no special qualities.

What has been said concerning the consumption of soap in wool scouring applies equally well in the similar processes of the silk and cotton industries. In the first process of silk manufacture the raw silk is soaked in a strong solution of soap containing neat's foot oil. This process is necessary to give the silk sufficient softness and pliability for the winding operation. With waters containing lime and magnesium in large amounts the soap forms the characteristic curdy precipitate, which mats the fibers and causes considerable difficulty in winding the silk. Furthermore, the precipitate clings to the fibers forming soap specks which later harden the silk at these points.

The next operation, that of boiling off, requires the use of greater quantities of both soap and water. The deleterious results of unsuitable water here are therefore intensified. Where lime spots form the silk may become discolored and the fiber crack. Weighting is largely affected by the lime and magnesium content of the water used in previous operations. Lime spots prevent the absorption of the tin solution at such points since the fiber is there covered by the sticky lime precipitate. The result is lack of uniformity in weighting and " hungry spots " which later in the dyeing operation produce uneven coloring of the fabric. Brighter colors are said to be produced with soft waters using less dye than with other waters containing large amounts of the alkali-earth radicles.

The cotton industry has long recognized the value of soft water in its operations. The boiling off requires the use of resin soap in large amounts which soap, like others, is wastefully consumed by calcium and magnesium in the water. The precipitates formed are resinates of calcium and magnesium which are just as troublesome in later operations as the corresponding oleates and stearates. Spots, difficult to wash out, dye, and bleach, are formed and a uniform white, so essential in this industry, is almost impossible to obtain. It is characteristic of silks and cottons produced by plants using soft water that the fabric has a softer " feel " not at all like the harsh " feel " of fabrics produced with waters containing large amounts of the hardening constituents.

The foregoing remarks concerning the quality of water as affecting the manufacture of textiles are sufficient to indicate the necessity for a clear, colorless, water containing as little calcium and magnesium as possible. The well-established treatment with lime and soda ash has been used with success in many plants and has much to recommend it. This is particularly true where free carbon dioxide, calcium and magnesium are present in very large amounts. The cost is low compared with some other processes and the results are satisfactory provided the treatment is carefully

regulated according to frequent and periodic analyses of the raw and treated water. As far as completeness of removal of hardness is concerned the method which is far superior to others is that in which artificial zeolites are used. Where the water contains only moderately high amounts of calcium, magnesium, and free carbonic acid this material should be carefully considered as a means of softening and even where such constituents are excessively high it can be used to good advantage as a finishing process to follow the lime-soda treatment. The result in either case will be a water so low in calcium and magnesium as to suit the most exacting demands of the woolen, cotton, or silk mill.

Essentially, the principles heretofore discussed with regard to soap consumption are applicable to the use of water in laundries.

Water for Use in Irrigating. An excess of alkali in the soil is detrimental to the growth of crops, and waters used in irrigation may seriously impair the fertility of land by augmenting its alkali content. Land would probably be injured by the best of natural waters if irrigated with them for a long period of time without natural or artificial drainage, for all irrigating waters contain alkali, and evaporation in and from the soil would result in a gradual accumulation of toxic salts. In order that waters may readily be compared with respect to their suitability for irrigation, a simple index of their irrigating value, such as the "alkali coefficient," is useful. The alkali coefficient is a purely arbitrary quantity intended solely to facilitate the comparison of waters to be used for irrigation. It may be defined as the depth in inches of water which, on evaporation, would yield sufficient alkali to render a 4-foot depth of soil injurious to the most sensitive crops. Thus, if the alkali coefficient of a water is found to be 17, 17 inches in depth of that water contains sufficient alkali to render injurious to sensitive crops the soil on which it is applied. Whether injury would actually result from the application of such a water to any particular piece of land, however, depends on methods of irrigating the crops grown, the character of the soil, and drainage conditions, and it should be clearly understood that the alkali coefficient in no way takes account of such conditions.

Hilgard [1] quotes results of investigations by R. H. Loughridge showing the greatest amount of various alkali compounds found in soils in which crops were not injured. About forty common cultures were included in the tables, and great diversity is indicated for the relative toxicity of the compounds toward the different cultures. The mean results for several cultures of about the same degree of sensitiveness, however, indicate with marked uniformity the relative toxicity of the alkalies toward common cultures to be about as follows: Sodium as Na_2CO_3, 10;[2] sodium as NaCl, 5;

[1] Hilgard, E. W., Soils, p. 467, 1906.

[2] The tables indicate a relative toxicity of about 6, but on account of the puddling effect of sodium carbonate on soils and the fact that the investigations did not distinguish between bicarbonate and carbonate of sodium, the value 10 is believed to be more satisfactory.

sodium as Na_2SO_4, 1. The investigations indicate further that about 1500 pounds per acre of sodium with a relative toxicity of 1 (as above) in 4 feet depth of soil is barely sufficient to affect injuriously the more sensitive common crops. The foregoing conclusions, being in accord with the results of other investigations, afford a basis for the calculation of the alkali coefficient, which may be made from a water analysis by means of the following formulas:

When rNa − rCl or Na − 0.65 Cl is zero or negative,

$$\text{Alkali coefficient, } k = \frac{288}{5\ \text{rCl}} = \frac{2040}{\text{Cl}}.$$

When rNa − rCl or Na − 0.65 Cl is positive but not greater than rSO_4 or 0.48 SO_4,

$$\text{Alkali coefficient, } k = \frac{288}{\text{rNa} + 4\ \text{rCl}} = \frac{6620}{\text{Na} + 2.6\ \text{Cl}}$$

When rNa − rCl − rSO_4 or Na − 0.65 Cl − 0.48 SO_4 is positive,

$$\text{Alkali coefficient, } k = \frac{288}{10\ \text{rNa} - 5\ \text{rCl} - 9\ \text{rSO}_4} = \frac{662}{\text{Na} - 0.32\ \text{Cl} - 0.43\ \text{SO}_4}.$$

In the foregoing formulas, the sodium and potassium value reported in many analyses may be used for Na; in the absence of a sodium or a sodium and potassium determination, Na may be estimated from the equations

$$\text{Na} = 0.41\ \text{HCO}_3 + 0.83\ \text{CO}_3 + 0.71\ \text{Cl} + 0.52\ \text{SO}_4 - (1.25\ \text{Ca} + 2.06\ \text{Mg})$$

$$\text{rNa} = 1.10\ [\text{rHCO}_3 + \text{rCO}_3 + \text{rCl} + \text{rSO}_4 - (\text{rCa} + \text{rMg})]$$

which for safety give a value about 10 per cent greater than the theoretical; and in the absence of calcium and magnesium determinations, the foregoing equations may be used if the parenthetical expression be replaced by one-half the total hardness (as $CaCO_3$) or its equivalent reacting value.

The first of the above formulas is applicable to waters that contain more chlorine radicle than is sufficient to combine with the sodium present, and involves the assumption that the other basic radicles required to hold the chlorine radicle in solution are as injurious as if replaced by their equivalent reacting value of sodium. The other formulas neglect possible injurious effects of basic radicles other than sodium. These assumptions, as applied to normal waters, are sufficiently accurate for practical purposes, though their application to soils might lead to serious errors.

Waters to which the first two formulas are applicable cannot be improved by chemical treatment, but are likely to produce only "white alkali" in the soil. Waters to which the third formula is applicable are likely to produce "black alkali" in the soil and can be improved to the alkali coefficient calculated from the second formula by the use of gypsum or "land plaster."

In general, injurious results from the use of a water for irrigation depend largely on drainage conditions and soil texture. Waters with low alkali coefficients may be used successfully on a loose soil with free drainage. The following approximate classification, which is based on ordinary irrigation practice in the United States, indicates in a very general way the customary limitations in the use of waters having various alkali coefficients:

CLASSIFICATION OF IRRIGATION WATERS

Alkali Coefficient.	Class.	Remarks.
More than 18..	Good	Have been used successfully for many years without special care to prevent alkali accumulation.
18 to 6.....	Fair	Special care to prevent gradual alkali accumulation has generally been found necessary except on loose soils with free drainage.
5.9 to 1.2.....	Poor	Care in selection of soils has been found to be imperative and artificial drainage has frequently been found necessary
Less than 1.2..	Bad	Practically valueless for irrigation.

Slow-sand Filtration. The art of purifying water by filtration has developed from a simple procedure on a small scale to a complicated and extensive process. Whereas individuals and industries were once content with a comparatively clear water, they now demand a product colorless, free from suspended impurities, as nearly sterile as efficient operation will produce, and free from such quantities and varieties of mineral constituents as will affect its use for a particular purpose.

The English, or slow-sand method of filtration, the first used on a large scale, employs a water-tight basin containing 5 or 6 feet of filtering material. A common practice is to use 3 feet of fine sand at the top of the filter bed, below that about a foot of coarser sand supported on about 18 inches of graded gravel, the coarser material at the bottom. Suitable drains are provided below the gravel to carry off the filtered water. Briefly the operation of a slow-sand filtration plant is as follows:

The raw water containing suspended impurities, clay, bacteria, and microscopic plants, flows into a sedimentation basin. The impurities in part settle to the bottom either by gravitation alone, or, in some installations, aided by the use of a coagulant that agglomerates the particles and hastens the settling. The partly clarified water flows from an outlet near the top of the basin to the filter bed, which, after accumulating a surface layer of impurities, passes an effluent substantially free from suspended matter, including bacteria, at the rate of about three million gallons per acre per day. When the surface layer, or *Schmutzdecke*, becomes so thick that the rate of filtration is too low for economical operation, the surface layer of sand is removed and washed, and later replaced. Length of operation without washing the sand may be increased substantially by raking the surface from time to time until it becomes so clogged that washing is

essential. The filtered water passes from the under drains to a clear water basin for storage and use.

This method is best suited to purifying waters of low turbidity on a large scale. It is used mostly for municipal water supplies.

Rapid-sand Filtration. The rapid-sand, or American system of filtration, is best adapted to the treatment of turbid and highly colored waters and is commonly employed where softening, as well as filtration, is necessary. The main differences between this and the English system are the artificial formation of a surface filtering layer on the sand by coagulation, the method of cleaning the filters by forcing a current of water, or air and water up through the filtering medium, and a much higher rate of filtration. Machines to apportion automatically the dose of chemicals to the flow of water are necessary. A mixing and reaction chamber is provided to secure the proper coagulation. The settling basin used in this type of plant is frequently deeper than that in the slow-sand type, and is provided with baffles designed to secure maximum settling in minimum time. Roughing filters, similar to the main filters but of coarser material, are frequently used to remove the greater part of the coagulated matter. The filters in a large installation consist of concrete basins (in smaller ones wooden or iron tanks) containing normally 30 inches of sand, on a foot of graded gravel, the gravel resting on perforated brass strainers through which the water passes to the drain system and thence to the storage basin. By reversing the flow of water through the strainers the water is forced up through the filter bed thoroughly stirring up the sand and washing the surface layer of impurities into channels provided to waste the dirty water. When the filter has been cleaned in this way the wash water is turned off and the sand settles back ready for the next period of filtration.

The operation of a typical plant where both softening and filtration are practiced on a large scale is as follows:

The raw water passes through a Venturi meter which records the volume of water passing and controls the rate of addition of coagulant to the flow of water. From the Venturi meter the water passes to a weir basin, thence to a set of weirs where the water is divided, one part going to the lime saturators for use in preparing the milk of lime, another over the soda weirs where the soda ash is introduced, and a third to the mixing tanks. The lime-saturated water, the raw water, and the soda solution are thoroughly mixed by a system of baffles in the mixing tank, and the greater part of the precipitated material is allowed to deposit in the settling basins. The filters remove the remainder, gradually clogging up and filtering more and more slowly. At the end of 8 to 12 hours' operation, clear water, sometimes aided by compressed air, is forced up through the strainers, the sand thus washed and prepared for another period of several hours' filtration.

Proper coagulation is a prime requisite in plants of this type. Some

waters contain sufficient iron to produce a good floc when lime is added, while others require the addition of filter alum, $Al_2(SO_4)_3$, but have normally sufficient alkalinity to precipitate the aluminum hydroxide without lime. Several large plants have found it more economical to make their own filter alum [1] by treating crude bauxite with sulphuric acid and using the mud or syrup directly for coagulation, thus obviating the necessity for crystallization, purification, etc.

Pressure Filters. Many industrial plants have found a type of filter that can be installed directly in the pressure water-supply system advantageous because of its low cost, ease of installation, small-space requirement, and flexibility in quantity of output. It has been further demonstrated that with the refinements of careful regulation and control of rate of filtration, addition of reagents, and systematic washing, these

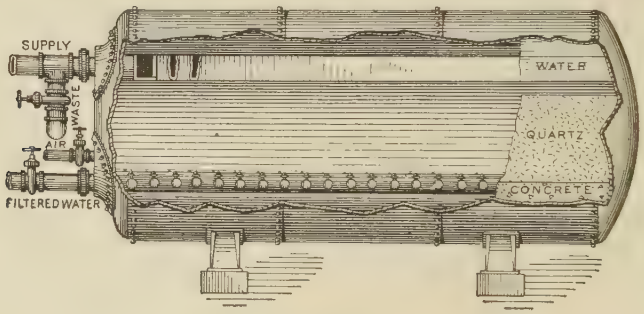

FIG. 55.

filters can produce an effluent comparable with many of the larger and more costly rapid-sand plants of the gravity type.

Pressure filters are usually stout steel tanks, cylindrical in form, placed either horizontally or vertically. The water is forced through the sand under pressure, but in other respects pressure filters differ but little in principle from the rapid-sand filters already described. A section of such a filter of the horizontal type is shown in Fig. 55.

By increased pressure, a pressure filter can more than double its output with little effect on the quality of the filtered water. This is a great advantage from an industrial standpoint. It has also been stated with at least some degree of truth, that combined with sterilization, a water can be produced which will meet most of the exacting demands of a domestic supply.

Drifting-sand Filter. The Ransome drifting-sand filter has the novel feature of continuous washing of the filter sand. Drain pipes are so arranged around the base of a cylinder that water carrying with it coagulated material and surface sand is constantly being drawn from the bottom of the filter, the sand washed and returned to the cylinder at the center of the

[1] *Engineering News*, Jan. 4, 1917, pp. 4–7.

top. This procedure makes the bed of sand take the form of a series of flattened cones (see Fig. 56).

Coagulant is used but there is no coagulating basin. The raw water, after proper treatment with alum, is passed through an ejector at the base of the sandwasher, where it picks up the clean sand and carries it to the top of the filter. About 98 per cent of the water passes through the stationary sand to a system of drains similar to a rapid-sand filter. The remaining 2 per cent is carried with the dirty sand out of the filter. In the plant installed at Toronto, Canada, it becomes necessary to back-wash the sta-

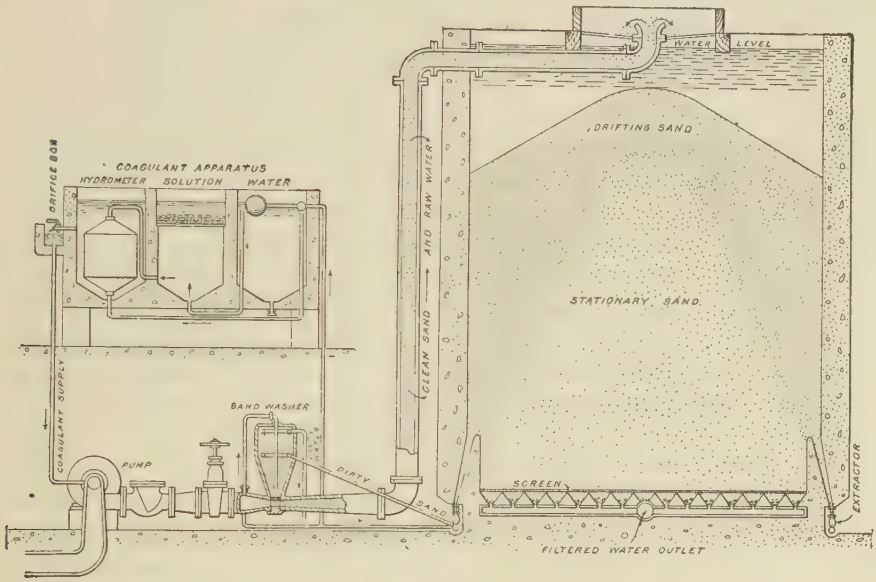

FIG. 56.

tionary sand about once a week. This is accomplished by the procedure usual for a rapid-sand filter.

It is claimed for this process that a bacterial efficiency equal to the ordinary rapid-sand process is secured with the same quantity of wash water and a much longer period of service.

Aeration. The cheap and plentiful reagent, air, applied to water in a simple manner does considerable toward purification. Iron can be oxidized and precipitated, carbon-dioxide can be eliminated, and disagreeable tastes and odors can be removed by this simple procedure. The devices to secure maximum mixing of air and water vary from simple cascades or falls to elaborate fountains with especially designed spraying nozzles. A common method is to force the water to flow from the upper end of a vertical pipe and drop down on boards placed beneath, causing the water to splash outward in all directions. Troughs over the edges of which the water spills are also much used. Where aeration is used to oxidize and precip-

itate iron, tricklers are often used to good advantage. These are porous beds of broken stone, coarse sand, coke, shavings, or similar insoluble material having a large surface as compared to its volume, through which the water slowly percolates. The air in such beds should be continuously or frequently changed, otherwise the process fails. Considerable attention is being paid of late to the design of spraying nozzles, possibly because of their extensive use in sewage purification. One type, installed at the Kensico reservoirs of the New York supply are cast with spiral vanes which impart to the water flowing through them a whirling motion, which should be effective in accomplishing aeration.

Sterilization by Calcium Hypochlorite. The treatment of water to destroy micro-organisms is chiefly employed as an adjunct to other methods of purification. It would seem unnecessary to provide such an extra precaution for filter plants which regularly operate with a bacterial efficiency of 98 per cent or higher, but when one considers that at times the total number of bacteria amounts to thousands per cubic centimeter the remaining 2 per cent constitute a figure of considerable magnitude. Then, too, no system is fool-proof, and occasional accidents or carelessness may allow the passage of water imperfectly purified, which may contain large numbers of disease-producing bacteria. A water supply thought to be safe from pollution and hence not purified by any process may suddenly become contaminated, spreading disease to thousands. These and other reasons, such as the destruction of organisms in water used for canning, brewing, etc., make necessary the sterilization of water.

The method most commonly employed on a large scale is to treat the water with a minute dose of bleaching powder or hypochlorite of lime, commonly designated "bleach" in the trade. This material is a mixed salt corresponding to the formula ($CaCl_2Ca(OCl)_2$). Purchase on specification is based largely on the percentage of "available chlorine" or percentage of chlorine which is available upon treatment with a strong acid. A customary figure is 35 per cent, which corresponds to a material containing about 62.5 per cent calcium hypochlorite. In solution the calcium chloride molecule is inert so far as sterilization is concerned, but the hypochlorite through a series of reactions gives, as final products, calcium chloride and nascent oxygen. Nascent oxygen liberated thus is a very effective germicide and it is due to its action and not the chlorine of the bleaching powder that sterilization is accomplished.

Chloride of lime is soluble in water in the ratio of about 1 to 20, but thorough mixing and a second treatment with water is necessary to extract the greater part of the active material from the sludge which forms. An excellent procedure is to use the water from the second extraction for the first extraction of the next lot of bleach. Whatever the method of solution, it is ordinarily made up so that one pound of chloride of lime is used for each 100 gallons of water and applied by means of a wide variety of methods at some point in the system of purification where the organic matter has

been reduced to the minimum and where a period of one-half to three or four hours can be given to allow the sterilizing action to go on. In a majority of small filter plants this point of application is just before the water enters the clear water basin, but in large plants this would necessitate great multiplicity of apparatus on account of the number of filters, each operating with a different rate. In plants of this kind the solution can be advantageously applied to the water in the lower end of the settling basin where a large part of the organic matter has settled out and some time will be given for the reaction before reaching the filters. Some of the taste due to hypochlorite will be removed by the filters, the filter sand will be sterilized, and " after-growths " of organisms in the sand and under-drains will be prevented.

As stated above, many methods are used to regulate the amount of sterilizing material added. Dry feed of the bleach by means of a spiral impelled by a water wheel operated at a rate which depends on the flow of raw water seems to be an efficient device. Where a solution is used, orifice boxes, proportional weirs, and auxiliary pumps with variable stroke directly connected with the main pump are sometimes installed. One of the best methods of securing accurate control is to adjust the strength of the calcium hypochlorite, after careful analysis, to a given strength and apply it in connection with a Venturi meter in such manner as to apportion automatically the amount of solution to the flow of water.

The amount of hypochlorite necessary to effect sterilization depends on the amount of oxidizable material present, the temperature, the allowable time of reaction, the period of storage, and the turbidity of the water. If the dose is too heavy, disagreeable tastes and odors will be left in the water, while if the dose is too light all the bacteria will not be destroyed. At many places excellent results are obtained with as little as 0.3 part per million of available chlorine, while under adverse conditions more than 2.0 parts per million are sometimes necessary.

Sodium-hypochlorite Sterilization. Sodium hypochlorite (NaOCl) is prepared as a solution by electrolyzing a solution of common salt. Like calcium hypochlorite, its efficiency as a germicide depends on its decomposition and liberation of nascent oxygen. It has been used for some time to a large extent in laundries for bleaching purposes but in waterworks only recently and in a few places.

Liquid Chlorine. Because of its many advantages liquid chlorine sterilization is being practiced in many of the newer plants. Its germicidal effects, like chloride of lime, are due to the liberation of nascent oxygen. The chemical reactions with water may be represented as follows:

$$Cl_2 + H_2O = HOCl + HCl.$$

$$HOCl = HCl + O.$$

Liquid chlorine may be purchased 99.8 per cent pure in steel cylinders containing about 100 pounds, at pressures which vary with the tempera-

ture from 50 to 200 pounds per square inch. Anhydrous chlorine is not corrosive but in the presence of a small amount of moisture it reacts vigorously with the ordinary materials of construction. This difficulty has been successfully overcome in several types of apparatus now in efficient operation by suitable valves which confine the water and water vapor to those parts of the apparatus constructed of non-corrosive material. These machines are constructed for either manual or automatic control and for direct application of the gas or a solution thereof. One type of apparatus

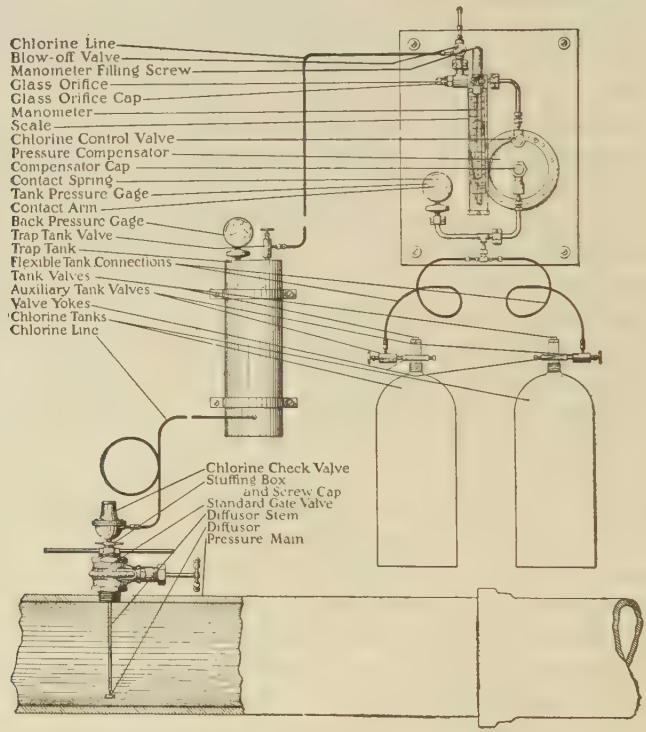

FIG. 57.

using solution feed is shown diagrammatically in Fig. 57. Its operation can be understood from the lettering.

The operation of the Dunwoodie Chlorinating plant capable of treating 400,000,000 gallons of water per day for the city of New York has been well described by Coffin.[1]

This plant has a total output capacity of a ton and a half of chlorine per twenty-four hours, the chlorine being applied automatically to the water by the direct-feed system through carborundum diffusors. Platform scales each with a capacity of ten cylinders are used to check by weight the

[1] Coffin, T. D. L., Chlorinating the Water Supply of Greater New York, *Eng. News*, Vol. LXXVI, No. 10, pp. 438–440, 1916.

delivery of chlorine. The apparatus was guaranteed to deliver within 5 per cent of the indicated chlorine and on checking with the scales was found to have an error of less than 1 per cent. The following advantages are claimed for liquid chlorine over chloride of lime treatment:

1. Greater efficiency and economy.
2. Liquid chlorine pure chemical.
3. A minimum space required for storage and operating.
4. Elimination of disagreeable odors and corrosive action in applying the disinfectant.
5. Liquid chlorine does not decompose.
6. Reactions simplified and more efficient at low temperatures.
7. A large overdose possible without producing tastes or odors in treated water.
8. More accurate control of feed.
9. No lime salts are introduced into the water.
10. A large saving in labor.

Ultraviolet Ray Sterilization. This, one of the latest developments in purifying water by sterilization, depends on the action of the invisible light rays emitted from an electric mercury vapor lamp immersed in the water to be sterilized. Details of construction vary but the more efficient types use a quartz tube with mercury electrodes, the whole separated from the water by a second quartz envelope which prevents cracking of the tube by differences of temperature between the water and the lamp. Baffles are arranged to secure repeated passage of the water in thin films past the source of light. The water must be clarified if turbid, otherwise the suspended matter may act as a protective medium shutting off the light from the bacteria to be destroyed.

Some of the more recent lamps have been fitted with arrangements whereby the water will, in case of an interruption of the current and the light going out, be automatically shut off and not turned on again until the lamp is lighted and has regained its maximum efficiency.

The advantages of this system are largely æsthetic. No chemical is added to the water and no tastes or odors are developed. The water can be heavily overdosed without affecting its quality, but cost of operation demands a very careful control to secure complete sterilization on the one hand and a reasonable current cost on the other.

Ozone. Although the ease with which this allotropic form of oxygen decomposes in the presence of organic matter liberating oxygen in the nascent state has been known for some time, it has been used for water sterilization on a large scale only since 1908. It is now used with success in many large plants, one at St. Maur (Paris) treating upwards of 25,000,000 gallons per day.

For efficient operation the air which is ozonized and later applied to the water must first be dried, conveniently by passing through towers of some desiccating material or by artificial refrigeration. The voltage

used in producing the silent discharge must not be allowed to rise too high, otherwise sparking occurs with a resultant waste of power, heat-decomposition of the ozone, and the formation of oxides of nitrogen that hinder the production of ozone. Efficiency furthermore demands a thorough mixing of the raw water and ozonized air with recovery of any ozone not absorbed in the mixing chamber.

Sterilization by Heat. Authoritative investigation has shown that water need not be boiled to destroy pathogenic organisms but that a temperature much below the boiling-point is sufficient to render the water sterile. A momentary exposure of water to a high temperature has been proven to effect sterilization and lower temperatures for longer periods are equally effective. Apparatus designed for small capacities operate by heating to boiling the upper part of a column of water, the ebullition carrying the water up and out of the tube down through tubes surrounded by the moving water which effects a heat exchange. The incoming water is thus heated and the boiled water cooled. The boiling lasts only a second or two, and it is claimed that the water thus treated retains its natural flavor with none of the insipid taste characteristic of boiled water. In large plants the principle of operation is somewhat different, circulation being effected by the expansion of a tall column of the liquid rather than active ebullition. Both types are automatically controlled so that no water can pass until it has been held at a sufficiently high temperature and length of time to insure the destruction of bacteria.

Feed-water Heaters. There are two types of feed-water heaters, open, or atmospheric, and closed. Both are used as a means of conserving heat and by chemical reactions due to heat effect a partial reduction in the scale-forming constituents of the boiler water. The closed heater consists of a steam- and water-tight vessel, containing tubes usually of brass or copper, on one side of which water is circulated and on the other steam. Whether the water is on the inside or outside of the tubes depends on the particular type designed. Both systems are used, the water tube more generally. The essential feature which distinguishes this heater from the open type is that when properly constructed to prevent leakage by too unequal expansion resulting from the cold water on one side of the tubes and the steam on the other, no mingling of steam and water takes place. The tubes are variously constructed to take care of this expansion difficulty, and considerable time and thought have been consumed in designing a connection at the tube ends between the tubes and the tube sheets. Metallic gaskets combined with composition packing are frequently used, giving a more or less flexible joint. Another means of overcoming the difficulty is to bend the tubes to form a U-shape. Still another method, and one which secures adequate baffling of the moving water, is to corrugate the tubes in a transverse direction, giving the appearance of a succession of bulges through which the water flows. Probably the best system, considering the large surface exposed for size of heaters and freedom from leakage, is a series of

coiled tubes. The water is made to circulate any number of times, depending on the design, and the steam is baffled by partitions in the shell to secure proper distribution of heat. Since the exchange of heat between steam and water must take place through the metal walls of the tubes, it follows that the efficiency of such a heater is a direct function of the conductivity of the tubes, the thorough breaking-up or circulation of the water, and the proper distribution of the steam in the heater.

The closed type of feed-water heater is used to good advantage where a soft water, containing but little scale-forming material is used, since the efficiency of the heater is seriously impaired by deposition of scale much as in a boiler. Such scale is more or less difficult to remove. On the other hand, using a soft water, the machine can be run a long time between cleanings. No trouble is experienced with oil in the feed water since the steam never comes in direct contact with the water. Simplicity of construction and operation are two of the outstanding features of the closed feed-water heater. Fig. 58 shows a closed heater of standard make.

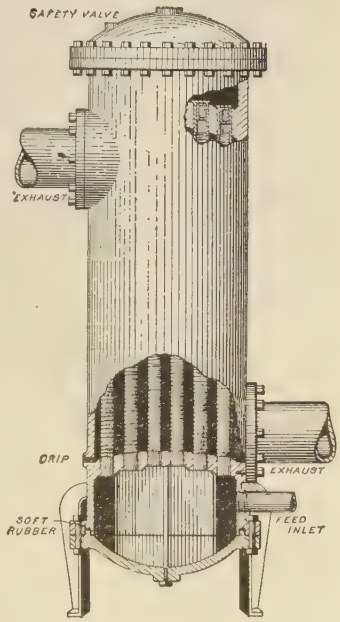

FIG. 58.

Open or Atmospheric Feed-water Heaters. The open heater differs from that of the closed type in that the steam comes in direct contact with the cold water. The apparatus is open to the air by means of a vent which allows the escape of gases liberated from the water. Steam purified by an oil filter, installed as a part of the heater, is allowed to blow between and around a series of removable trays arranged one above the other in such way that the water is showered down like rain. The heated water falls to a hot well in the bottom of which is located a filter for the removal of suspended particles. The condensed steam becomes mixed with the heated water and thus distilled water is added to the system. Automatic control is secured by properly constructed valves. The sectional view (Fig. 59) clearly shows the construction of such a heater. Because of the more efficient heat exchange, higher temperatures are obtained in heaters of this type with more complete removal of gases, and scale-forming constituents. The gases escape through a vent at the top. Scale deposited on the trays is removed periodically by removing and scraping the trays. Precipitates formed and matter in suspension are removed by the filter which should also be cleaned at proper intervals. The ready manner in which precipitated and deposited impurities are disposed of permits the use of a feed water higher in scale-forming constit-

uents than does a closed heater, but it should always be remembered that heat alone will not efficiently purify a water for boiler use, and a feed-water heater is not in itself primarily a water-purifying system.

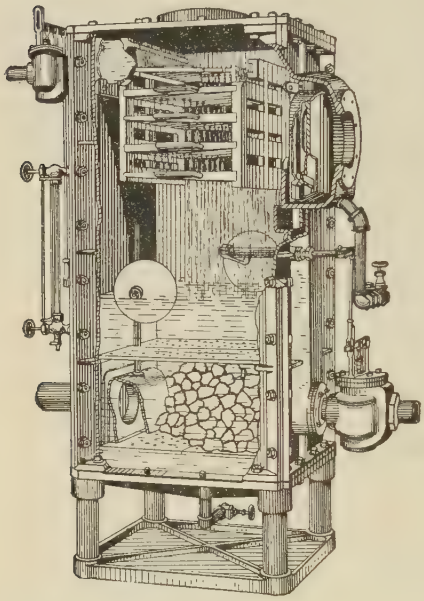

Fig. 59.

Regarding the reactions which go on when feed water is heated by steam as described above, it may be said that virtually the same reactions take place in both the open and closed heaters. The completeness is another matter and depends on the time allowed for reactions, the temperature that the water attains, and the amount and nature of the impurities present. In general, the open heater secures better results since the temperature is apt to be higher in this type.

The first noteworthy effect in an atmospheric heater is the escape from the water of dissolved gases. According to Smith [1] the evolution of gases absorbed from the atmosphere begins at about 67° C. (120° F.) and slowly increases in intensity up to about 88° C. (190° F.). Further heating produces a very rapid increase in gas evolution until at the boiling-point the expulsion is very nearly complete. In atmospheric heaters, therefore, complete removal of dissolved gases is the first step in purification.

The changes which follow appear to depend upon the relations which the basic radicles bear to the bicarbonate and carbonate radicles in the presence of water at various temperatures. Aluminum, even in the cold, rapidly precipitates as the hydrate with liberation of carbon-dioxide under these conditions. This is the action depended upon for coagulation with aluminum sulphate previously noted. It is so rapid and complete that it is safe to assume that aluminum radicle will never be present in a system of dissolved solids containing carbonate or bicarbonate radicles. In hot water iron acts similarly, though more slowly, if oxygen also is present. In the absence of oxygen a carbonate of iron precipitates. The removal of iron is, however, a comparatively unimportant action of the feed-water heater. The complexity of the results obtained by heating a solution containing only magnesium, carbonate, and bicarbonate radicles has been shown by Davis.[2] He found that magnesium carbonate is the only precip-

[1] Smith, James Alexander, *Engineering*, Vol. LXXVIII, 1904, p. 486.

[2] Davis, W. A., Studies of Basic Carbonates, Jour. Soc. Chem. Ind., Vol. XXV, 1906, p. 788.

itate caused by heating at temperatures less than 78° C. (172° F.). From this temperature to the boiling-point a mixture of carbonates and the hydrate was precipitated. Finally, prolonged boiling produced a continued precipitation of magnesium hydrate. Some magnesium was found in solution even after boiling 75 minutes. This complexity has rendered difficult estimates of the completeness of the precipitation as measured by the solubility of magnesium.

Engel and Ville [1] have, however, established the fact that magnesium is practically insoluble in the presence of carbonate or bicarbonate radicles at boiling temperature under atmospheric pressure. This condition is only reached by prolonged boiling and at slightly lower temperature the solubility is increased beyond the magnesium content of ordinary waters. A partial precipitation of magnesium radicles in an atmospheric feed water heater is, therefore, to be expected, but such precipitation will probably never be complete, will vary greatly with slight temperature changes, and cannot be depended upon to reduce materially the magnesium radicles present in the water. This is corroborated by practical results of such heaters. Calcium, though easily soluble at ordinary temperatures, forms the nearly insoluble calcium carbonate at 100° C. (212° F.). Considerable time is required to make the action complete so the figure established by Le Blanc and Novotny [2] (8.3 parts per million of calcium soluble in the presence of bicarbonate or carbonate radicles at 95° C. to 100° C.) may be increased to 15 parts per million of calcium for practical use in connection with the atmospheric feed-water heater. Sodium and potassium are very soluble in the presence of carbonate or bicarbonate radicles and all these radicles may be found in solution at high temperatures after iron, calcium, and magnesium have been precipitated.

The precipitates formed as indicated above act as coagulants and carry down with them a portion of the suspended and colloidal matter in water. The reduction is variable but complete removal of suspended matter and 20 per cent removal of colloidal matter may be usually expected with the atmospheric heater.

Sealed heaters are less effective than atmospheric in purifying water because the dissolved gases are not allowed to escape and because the somewhat lower temperature and higher pressures usually encountered with this type result in decreased precipitation.

The purification effected by heaters will depend, in addition, upon the settling space or filtration devices provided for precipitates. In connection with atmospheric heaters, the use of chemical precipitants, properly

[1] Engel, P. and Ville, J., Sur la solubilité du carbonate de magnésie dans l'eau chargée d'acide carbonique, *Compt. Rend.*, Vol. XCIII, 1881, p. 340.

Engel, R., Sur la dissolution du carbonate de magnésie par l'acide carbonique, *Compt. Rend.*, Vol. C, 1885, pp. 352 and 444.

[2] Le Blanc, M., and Novotny, K., Über die Kaustizierung von Natriumkarbonat und Kaliumkarbonat mit Kalk, *Zeit. anorg. Chem.*, Vol. LI, 1906, p. 181.

applied, will produce a very high degree of purification of boiler feed water. In such case the heater is in effect a hot system water-softening plant.

Boiler Compounds. Boiler compounds are substances or mixtures of substances which are added to feed water for the purpose of preventing the formation of hard scale in boilers. The variety is wide and their number countless, but all are supposed to act either mechanically to mingle with the scale and prevent cementing or chemically to produce a flocculent precipitate in the boiler. The danger of using such substances as graphite, clay, talc, etc., comes from the possibility that they may lump together or settle in a mass on the tubes or crown sheets, causing overheating with its attending results. Even presuming they do form a film over the surface of the tube so that the scale cannot adhere, all these substances are heat insulators and little is gained by substituting a coating of this kind for the scale itself. Fats, starches, wood extracts, tannates, and other organic materials used with discrimination have some value as boiler compounds. Their action is reasonably explained by the theory of "protective colloids." This theory applied to the action of such substances states that changes which substances in an extremely fine state of division undergo, namely from suspension to a fine, soft flocculent precipitate growing in size by absorption or cohesion, uniting more and more firmly together and gradually hardening to a crystalline state, may be prevented before the hardening stage by the use of other colloids which inhibit the change. This theory has more or less scientific backing, and use of such curious compounds as old leather or an oak board may have real foundation in reason. The compounds which act chemically to precipitate incrustants are better understood, can be adjusted to suit any average condition, and they are therefore more reliable agents when made up according to the analysis of the water treated and used according to directions. Sodium carbonate, sodium hydroxide, sodium phosphate, alkaline silicates, barium salts, chromates and oxalates, and mixtures of two or more of these substances are used. The result should be a soft non-adhering scale which can be removed from time to time by blowing-off.

At best the use of boiler compounds is but a partial substitute for softening feed water. Where installations are small they may be used to advantage. In general their use may be likened to the administration of certain varieties of rat poison which, although effectively causing the termination of the rodent's mortal existence, yet make necessary the rather difficult and troublesome removal of his earthly remains.

Water Softening. Water softening consists in adding chemicals to the water to precipitate its hardening constituents, subsidence to remove the greater part of the precipitate thus formed, and filtration to effect a more complete clarification. Under present practice, the entire softening process is carried out almost automatically in specially constructed water-softening machines, one type of which is described on page 93. An analysis of the water to be treated indicates approximately the quantity

and kind of chemicals that should be added and the machine is adjusted to add them automatically.

The hardening constituents of water, those which will decompose soap, are the iron, aluminum, calcium, magnesium, and hydrogen radicles. The dissolved gases, carbon dioxide and hydrogen sulphide, may act similarly to a slight degree, because they give rise to the presence of hydrogen radicles when dissolved in water. The chemicals customarily used for softening are lime, CaO, slaked and added as calcium hydroxide, $Ca(OH)_2$, and soda ash, Na_2CO_3. By their aid the greater part of the suspended and colloidal matter, carbon dioxide, hydrogen sulphide, and the iron, aluminum, calcium, magnesium, hydrogen, carbonate, and bicarbonate radicles of the water are removed. Lime alone will usually remove the greater part of these impurities, but for more complete reduction of calcium soda ash is often used. There are other chemicals that will accomplish the same results as lime and soda ash, some of them with more effectiveness and convenience, but the relative cheapness of those named has resulted in their almost exclusive use for softening purposes.

The principles of water softening are comparatively simple. The two substances which it is generally most desirable to remove are calcium and magnesium. The former will be precipitated in the presence of carbonate radicles (CO_3), and the latter will pass out of solution in the presence of hydroxyl radicles (OH). To soften water, therefore, it is only necessary to provide an excess of CO_3 and OH. Soda ash, Na_2CO_3, will furnish CO_3; and slaked lime, $Ca(OH)_2$, will furnish OH directly, and by reaction with CO_2 and HCO_3 will furnish CO_3 also.

Upon adding soda ash to a water, carbon dioxide, hydrogen sulphide, iron, aluminum and hydrogen radicles appropriate the first of the CO_3, but, because these radicles are not often present in great amount, little soda ash is required for them. The reactions may be assumed to take place as follows:

$$\begin{aligned}
CO_3 + CO_2 + H_2O &= 2\,HCO_3;\\
CO_3 + H_2S &= HS + HCO_3;\\
CO_3 + Fe &= FeCO_3;\\
3\,CO_3 + Al + 3\,H_2O &= 3\,HCO_3 + Al(OH)_3;\\
CO_3 + H &= HCO_3.
\end{aligned}$$

The iron and aluminum compounds thus formed are precipitated. The bicarbonate radicle, together with the sodium radicle which is added, passes into the chemical system of dissolved solids.

The next result of adding soda ash is attended by the appropriation of CO_3 radicles by calcium, thus:

$$CO_3 + Ca = CaCO_3.$$

Most of the calcium carbonate thus formed falls as a precipitate, sodium taking the place of calcium in the system of dissolved solids. This pre-

cipitation of calcium is never complete. In water free from other radicles, 5.2 parts [1] per million of calcium will remain in solution in the presence of carbonate radicles at ordinary temperature. In water-softening practice this minimum limit is very seldom reached. The content of calcium in softened waters may be as high as 20, but will average about 12 parts per million. The addition of soda ash in excess of that required by the foregoing reactions will tend to make the precipitation of calcium a maximum, removing, however, only a few additional parts per million. No other softening action is obtained by an excess of soda ash. When slaked lime, $Ca(OH)_2$, is added to a water, it supplies OH radicles which are first appropriated by carbon dioxide and hydrogen sulphide and iron, aluminum and hydrogen radicles, thus:

$$2\,OH + CO_2 = CO_3 + H_2O;$$
$$OH + H_2S = HS + H_2O;$$
$$2\,OH + Fe = Fe(OH)_2;$$
$$3\,OH + Al = Al(OH)_3;$$
$$OH + H = H_2O;$$

These minor changes result in precipitation of iron and aluminum. Their place in the system of dissolved solids, however, is taken by the added calcium, so that no softening is accomplished. A further addition of $Ca(OH)_2$ results in the appropriation of OH radicles by the HCO_3 and Mg radicles, as follows:

$$OH + HCO_3 = CO_3 + H_2O;$$
$$2\,OH + Mg = Mg(OH)_2.$$

The first of these reactions provides CO_3 which, in turn, precipitates Ca as indicated in the case of soda ash. If the water originally contains sufficient HCO_3 radicle to react with all the Ca, the calcium content may thus be reduced to about 28 parts per million before the second reaction takes place in any notable degree. A further addition of lime brings the second reaction into greatest prominence and results in precipitation of magnesium to its practical minimum value of about 5 or 6 parts per million at ordinary temperatures. In the presence of an excess of HCO_3 the first reaction also continues, so that both magnesium and calcium may be reduced to a minimum. In the absence of HCO_3 radicle the precipitation of magnesium is accompanied by an equivalent increase in calcium and the addition of soda ash becomes necessary for maximum softening.

Consideration of the foregoing reactions and their results makes it possible to calculate with a considerable degree of accuracy the quan-

[1] Le Blanc, M., and Novotny, K., Über die Kaustizierung von Natriumkarbonat und Kaliumkarbonat mit Kalk; *Zeit. anorg. Chem.*, Vol. LI, p. 181, 1906.

Whipple, G. C., and Mayer, A., Jr., The Solubility of Calcium Carbonate and of Magnesium Hydroxide and the Precipitation of these Salts with Lime Water; Reports and Papers of the Am. Pub. Health Assoc., Vol. XXXI, Part 2, p. 151, 1905.

tities of lime and soda ash to be used for partial or maximum softening of waters. In terms of reacting values and also in terms of pounds per thousand gallons, these quantities of lime and soda ash are given in the following formulas:

Maximum softening, including removal of CO_2, H_2S, Fe, Al, H, all but about 12 parts per million of Ca, and all but about 5.5 parts per million of Mg, obtained by use of lime and soda ash in conjunction applied as follows:

(*a*) Pounds 90 per cent lime required per 1000 gallons

$$=0.26\ (rFe+rAl+rMg+rH+rHCO_3+0.0454\ CO_2+0.0294\ H_2S)$$
$$=0.00931\ Fe+0.0288\ Al+0.0214\ Mg+0.258\ H+0.00426\ HCO_3$$
$$+0.0118\ CO_2+0.00763\ H_2S.$$

(*b*) Pounds 95 per cent soda ash required per 1000 gallons

$$=0.465\ (0.0294\ H_2S+rFe+rAl+rCa+rMg+rH-rCO_3-rHCO_3)$$
$$=0.0137\ H_2S+0.0167\ Fe+0.0515\ Al+0.0232\ Ca+0.0382\ Mg$$
$$+0.461\ H-0.0155\ CO_3-0.00762\ HCO_3.$$

Softening with soda ash alone, removal of CO_2, H_2S, Fe, Al, H, and all but about 12 parts per million of Ca can be accomplished with the following dose of soda ash:

(*c*) Pounds 95 per cent soda ash required per 1000 gallons

$$=0.465\ (0.0454\ CO_2+0.0587\ H_2S+rFe+2rAl+rCa+2rH)$$
$$=0.0211\ CO_2+0.0273\ H_2S+0.0167\ Fe+0.103\ Al+0.0232\ Ca$$
$$+0.923\ H.$$

Softening with lime alone to secure maximum removal of magnesium requires the use of the dose shown in formula (*a*). By this dose removal of CO_2, H_2S, Fe, Al, H, is accomplished and all but about 5.5 parts of magnesium may be removed. Whether calcium is increased or reduced will depend upon the content of CO_3 and HCO_3 in the water. If it is desired to secure a partial softening with respect to calcium only, removal of CO_2, H_2S, Fe, Al, H, and an economic maximum of Ca can be accomplished as follows:

Case 1. rCO_3+rHCO_3 greater than rFe+rCa. Use dose of formula (*a*) omitting terms containing Mg and HCO_3 and adding the term rCa (or 0.0130 Ca in the second form).

Case 2. rCO_3+rHCO_3 not greater than rFe+rCa. Use formula (*a*), omitting terms containing Mg.

The use of soda ash to supply CO_3 radicles for water-softening results in an increase in the highly soluble constituents, for the sodium thus added remains in solution. In some industrial uses of water a great increase in content of sodium is accompanied by very undesirable effects. In such cases it may be necessary to use in place of soda ash some carbonate whose base will not be held in the dissolved system by SO_4 or Cl radicles. No commercial compound that will wholly fulfill these condi-

tions has been used. Barium, Ba, however, will not remain in solution with SO_4 radicle. Barium carbonate, $BaCO_3$, therefore possesses a distinct advantage over soda ash in the treatment of highly sulphated waters. It is itself nearly insoluble but can be added to the water in suspension, any excess above the amount required for the reactions being removed with the precipitate. It has the disadvantage of a comparatively high price. Lime, soda ash, and barium carbonate can be used in conjunction for softening as follows:

Lime: Dose shown by formula (*a*).

(*d*) Minimum dose pounds of 95 per cent soda ash per 1000 gallons

$$=0.465\ (rCl+rNO_3-rNa-rK)$$
$$=0.0131\ Cl+0.0075\ NO_3-0.0202\ Na-0.0119\ K.$$

If the dose thus calculated be negative, no soda ash is required. This will generally be the case. The dose as calculated may be increased at will, the point in such increase being to keep the value of the expression $Na+K+0.435$ *soda ash* below the allowable maximum of $Na+K$ in the particular industrial use for which the softening is undertaken.

(*e*) Barium carbonate required, pounds per 1000 gallons

$$=0.8225\ (0.0294\ H_2S+rFe+rAl+rCa+rMg+rH-rCO_3-rHCO_3-2.15\ \textit{soda ash}).$$
$$=0.0242\ H_2S+0.0295\ Fe+0.0910\ Al+0.0411\ Ca+0.0676\ Mg+0.816\ H-0.0274\ CO_3-0.0135\ HCO_3-1.77\ \textit{soda ash}.$$

By the term "soda ash" in formula (*e*) is meant the dose of 95 per cent soda ash, in pounds per 1000 gallons, actually used in treating the water.

The quantities of chemicals given above are based upon the reactions that would theoretically take place in water softening. They have, however, been tested by computations upon many practical softener installations and have been found to be substantially correct. They can safely be used for estimating cost of chemicals for softening and for starting water treatment. The results of treatment may in some cases warrant a slight change of the calculated dose.

Successful softening machines are so designed that the chemicals and water are thoroughly mixed, that adequate time for the reactions is allowed, that a suitable sedimentation compartment is traversed by the water before filtration, that a final rapid filtration will remove all remaining traces of matter in suspension. Neglect of any one of these features will make the best results incapable of attainment. If the reactions are incomplete when the water leaves the softener, "after deposits" of precipitates are likely to occur, causing much trouble. To prevent this, softened waters are sometimes treated with carbon dioxide, which will hold in solution the calcium and magnesium which would otherwise form after deposits. This practice is to be commended as a preventive of

deposits in the cold, but the material is thrown down in any case when the water is heated and the addition of carbon dioxide increases the corrosive action under some conditions. Carbonating softened water is, therefore, by no means a practice devoid of deleterious results.

Softened water has many applications in the industries. It is also used for drinking purposes, for which it is doubtless better suited than many of the untreated waters. Inasmuch as barium salts are poisonous in comparatively small quantities, however, water treated with the carbonate or other salts of barium cannot be drunk with assured safety.

The completeness of maximum softening of water is remarkably uniform. With more perfect regulation of the chemical dose and subsequent softening operations, even greater uniformity would be attained. The following tables illustrate the uniformity secured in practical softening

TABLE 1.—PER CENT OF WATERS HAVING SPECIFIED MINERAL CONTENT BEFORE AND AFTER SOFTENING

Parts per Million.	Suspended Matter.		Silica (SiO_2).		Iron Oxide and Alumina ($Fe_2O_3+Al_2O_3$).		Free Carbon Dioxide (CO_2).		Calcium (Ca).		Magnesium (Mg).	
	Before	After	Before	After	Before	After	Before	After	Before	After	Before	After
Less than 5	53	96	7	24	64	84	12	100	0	0	4	62
5 to 9.9	7	2	26	28	25	16	12	0	0	34	13	30
10 to 19..	7	0	15	20	7	0	16	0	2	64	34	6
20 to 29..	5	0	24	13	2	0	15	0	4	2	15	2
30 to 39..	7	0	15	7	0	0	3	0	9	0	15	0
40 to 49..	5	2	11	4	2	0	12	0	6	0	7	0
50 to 74..	12	0	2	4	0	0	6	0	34	0	6	0
75 to 99..	0	0	0	0	0	0	9	0	15	0	2	0
100 to 199.	0	0	0	0	0	0	9	0	24	0	4	0
200 to 499.	2	0	0	0	0	0	6	0	4	0	0	0
500 to 1000	2	0	0	0	0	0	0	0	2	0	0	0

TABLE 2.—MAXIMUM, MINIMUM, AND MEAN VALUES FOR SPECIFIED MINERAL CONSTITUENTS BEFORE AND AFTER SOFTENING

(Parts per million)

Constituents.	Maximum.		Minimum.		Mean.		
	Before.	After.	Before.	After.	Before.	After.	Per Cent Reduction.
Suspended matter.....	959	40[1]	0	0	41	1.1	98
Colloidal matter.....	74	.....	5.8	2.1	26	18	31
Silica (SiO_2).....	68	58	2.7	2.1	22	16	27
Iron oxide and alumina ($Fe_2O_3+Al_2O_3$).....	40	8.9	Trace	0	4.8	2.1	56
Free carbon dioxide (CO_2).	238	0	1.7	0	49	0	100
Calcium (Ca).....	581	21	12	5.1	103	12	88
Magnesium (Mg).....	156	27 [1]	1.3	.6	28	5.2	82

[1] Dose not such as to produce even an approximation to complete softening. With this exception maximum is 9 for suspended matter and 13 for magnesium

installations and includes the results of treating 47 miscellaneous waters, the dosing of which was not in all cases such as to produce maximum softening. The analyses represent two different types of softening machines and were made at 12 different laboratories. They are believed, therefore, to be fairly representative.

From these tables, it appears that suspended matter and free carbon dioxide are completely removed by softening; calcium and magnesium are reduced to 12 and 5.2 parts per million, respectively; colloidal matter is reduced by about 30 per cent, including about 25 per cent reduction in silica and 50 per cent reduction in iron oxide and alumina. Silica shows the least reduction, but the detailed analyses from which these tables were prepared indicate that the silica found in the softened water is in great measure derived from the glass of the bottles in which the water was stored previous to analysis. It is believed, therefore, that 50 to 75 per cent of colloidal matter will ordinarily be removed in softening. In the absence of definite proof, however, the figures first cited had best be taken as the average performance of the water softener. Of the acid radicles, the bicarbonate is completely removed and the carbonate reduced to about 30 to 40 parts per million with complete softening. If barium carbonate be used, the sulphate radicle may be removed completely.

Water Softeners. The recognized standard method for the proper treatment of waters for boiler purposes is that of adding to the water, in tanks designed for the purpose, certain chemicals in proportion to the amount and nature of the ingredients to be removed and the volume of water treated. The major portion of the precipitate formed is allowed to settle and the rest is removed by filtration. When properly controlled by chemical analysis of the raw and treated water, the chemicals added, and operated in accordance with the results, this method can be made to satisfy all ordinary conditions.

There are two general types of such softeners—one known as the cold process, the other using the beneficial effects of heat to hasten and complete reactions, called the hot process. Cold-water softeners may be further divided into intermittent and continuous.

The intermittent system employs tanks operating in pairs. They are filled alternately with water; while one is filling the reagents are introduced and thoroughly mixed by mechanical stirring devices usually rotating paddles. Settling is hastened by stirring up the particles from a former treatment, which particles act as nuclei upon which precipitation may start and larger crystals form. By the time the tank is filled all the reagent has been added, the stirring device is stopped, and the precipitate allowed to settle. The softened water is drained from near the surface by means of a floating hinged pipe, so arranged that as the level of the water is lowered neither the surface scum nor the precipitate at the bottom is allowed to pass through. This materially lessens the duty of the filter through which usually the water next passes before use. While

one tank is being thus used for reaction and settling, the other is supplying treated water, the process being so regulated that a constant supply of soft water is always available. Sludge is disposed of when necessary by simply opening a sludge gate at the bottom of the tank and starting the stirring device. It is claimed for this type of softener that since definite quantities of water are treated each time and the exact amount of chemicals weighed out, it is possible to treat more accurately any water no matter how it may vary in quality.

Continuous Water Softener. The essential feature of this type as distinguished from the intermittent is a continuous feed of raw water and chemicals and a resulting uninterrupted flow of treated water from the softener. The details of construction, as with many machines, vary to a considerable extent. A typical softener is here described but many others equally efficient might have been selected as examples. Fig. 60 shows a sectional view and general arrangements of the apparatus.

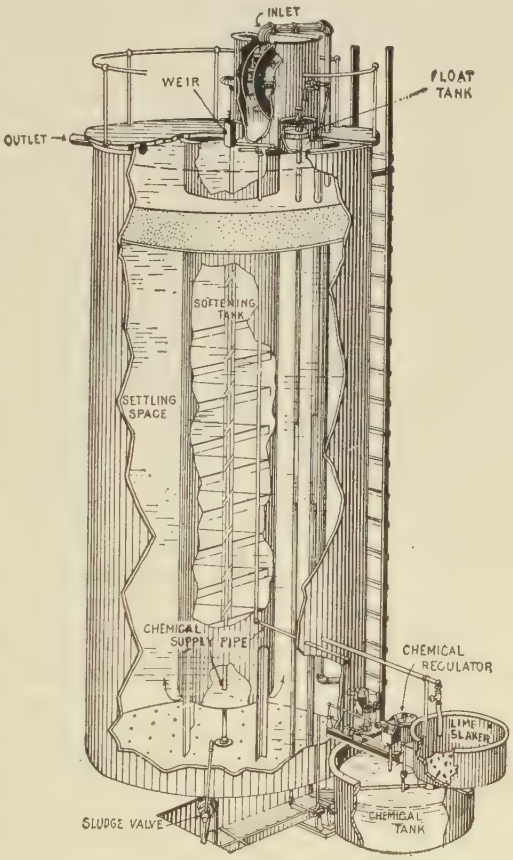

Fig. 60.

This softener is operated from the ground level where the preparation and mixing of the reagents can be readily inspected and controlled. The tanks are usually built of steel. The raw water is pumped to the top of the softener and allowed to flow upon an over-shot wheel which furnishes all the power necessary to operate the mixing devices and chemical pumps. From the wheel the water passes over a raw-water weir into the top of the mixing chamber where it is treated with the proper quantity of chemicals, which is regulated and operated by the flow of raw water. The mixing chamber is provided with a vertical shaft on which are mounted a large number of paddles to secure vigorous stirring and intimate mixture of water and reagents. From the open bottom of this chamber the softened water slowly rises, allowing sufficient time for the precipitate to settle to

the bottom of the softener from which it is periodically flushed by opening a sludge valve provided for this purpose. By the time the softened water has reached the excelsior wood-fiber filter it should be practically free from suspended particles, but the filter is used to remove any that may remain.

The advantages of the continuous softener lie mainly in its large output for small space required for installation, and little labor and attention required in operation.

Hot-process Water Softeners. The effect of heat in hastening and completing chemical reaction is taken advantage of in the so-called "hot-process" water softeners. Except the addition of an arrangement for chemical feed, construction and operation of these devices differs but little from open feed-water heaters.

When properly designed and operated to give adequate time for reaction, high enough temperature, automatic and accurate control of chemical feed, and proper filtration, this type of softener has several advantages worthy of mention. In the first place, they perform all the functions of an open feed-water heater, using exhaust steam, occasionally with some live steam to secure adequate heating. A decided saving in coal is thus effected. Condensed exhaust may be returned to the softener with a resulting decrease in quantity of raw water to be treated. The use of only one reagent, soda ash, simplifies and hence tends to easier and better regulation of the chemical treatment.

Proper heating effects the complete removal of the free carbon dioxide and temporary hardness. The quantity of chemical necessary for purification is thus materially reduced. The accelerating action of the higher temperature has already been mentioned, and to this may be added that the reactions tend to go farther toward theoretical completion. The precipitates formed are more coarsely granular and hence settle more rapidly and completely.

Attention must be directed to the fact that the above statements apply only to softeners properly designed, properly cared for, and operated reasonably close to the rated capacity.

Permutit. One of the more recent and most important developments in the art of water softening has been in the use of permutit. This material, an artificial zeolite having the formula $2\,SiO_2 \cdot Al_2O_3 \cdot Na_2O \cdot 6H_2O$, is insoluble in water but reacts with the calcium and magnesium of waters by exchange for an equivalent quantity of sodium from the permutit. A great advantage over other processes is due to the ready regeneration of the material by simply saturating the exhausted mass with a solution of common salt. Typical softening reactions are as follows:

$$Na_2(Al_2Si_2O_8) + Ca(HCO_3)_2 = Ca(Al_2Si_2O_8) + 2\,NaHCO_3;$$

$$Na_2(Al_2Si_2O_8) + MgSO_4 = Mg(Al_2Si_2O_8) + Na_2SO_4.$$

The regeneration reaction may be represented by the equation:

$$Ca(Al_2Si_2O_8)+2\,NaCl=Na_2(Al_2Si_2O_8)+CaCl_2.$$

A sectional view of a permutit filter is shown in Fig. 61. A prefilter is shown in the tank above the permutit bed. Its purpose is to remove suspended matter which would clog the pore spaces of the permutit. This, with its connections and a salt solution tank, are the only requisites in the line of apparatus. The water passes through the prefilter at the top of the pressure tank percolates through the permutit, is softened and flows into a space below. When the permutit has become exhausted a solution of common salt is allowed to flood the softening material from below and after a proper period washed out and the permutit is again ready for service.

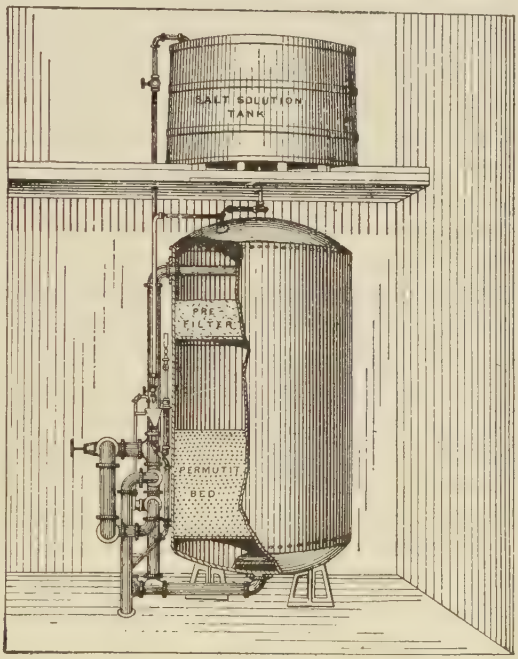

Fig. 61.

The advantages of this process are many. It produces a water of zero hardness, is simple to operate, requires little space, is flexible in operation, automatically takes care of variation in hardness of raw water, and forms no sludge. However, attention must be called to the following points:

The softened water contains in every case a higher concentration of sodium salts than the raw water, and the cost is greater than the lime-soda method.

Distillation. Conditions exist where softening, filtration, and many other purification processes are of no avail. Certain industries must have an absolutely pure water, and in some localities no water fit for domestic or industrial use is available. Under such conditions distillation is the only resort. Christie describes the process as follows:[1]

"One method of producing pure distilled water is that in which the apparatus introduces live steam into a closed tubular condenser at a

[1] Christie, William Wallace, Water its Purification and Use in the Industries: D. Van Nostrand Co., N. Y., 1912.

pressure of from 50 to 100 pounds per square inch by gauge, preferably the higher pressure. The steam is condensed by means of a water jacket at a lower pressure than is maintained in the condenser itself. This condensation generates some steam in the water jacket. This steam is carried into the condenser of the next effect and the process is again repeated and continued—a certain drop in pressure is automatically maintained between each pair of effects, by reinforcing heat to compensate for that lost by radiation, resulting in a high degree of efficiency.

"The distilled water is drawn from the several condensers. With this device it is said to be possible to obtain as high as ten gallons of water with one pound of coal burned. Water thus prepared is said to taste like spring water. The gases generated and contained in the steam not coming in contact with the water, the insipid or boiled water flavor is absent.

"The remaining steam from the last condenser may be used at its reduced pressure to run engines, or for heating, cooking, laundry purposes absorption ice machines, etc.

"Equally good results are obtained from sea or alkaline waters."

High cost of installation and operation is the main disadvantage of this process, but where a high degree of purity is an absolute necessity cost may become a secondary consideration.

Applications. The foregoing formulas relating to value of water in steam-making and in irrigation and in water-softening will now be applied to a few analyses, the results of calculation of the various formulas presented and classification of the waters in accordance therewith being given below:

ANALYSES OF WATERS AND RESULTS OF FORMULAS

(Parts per million)

	Weights.					Reacting Values.				
	A.	*B.*	*C.*	*D.*	*E.*	*A.*	*B.*	*C.*	*D.*	*E.*
1. Suspended matter....	30.00	118.00	0.00	14.00	0.00					
2. Colloidal matter.....	3.07	9.36	11.23	13.60	10.80					
Silica (SiO_2).....	3.00	6.80	11.00	11.00	6.50					
Iron oxide (Fe_2O_3)..	.07	.06	.23	2.60	4.30					
Alumina (Al_2O_3)....	....	2.50								
3. Dissolved gas:										
Carbon dioxide (CO_2).	10.00	.00	7.50	....	122.00					
4. Dissolved radicles:										
Calcium (Ca).....	11.00	16.00	64.00	8.30	28.00	0.55	0.80	3.19	0.41	1.40
Magnesium (Mg)...	2.80	4.20	12.00	1.80	12.00	.23	.34	.98	.15	.98
Sodium (Na).....	4.60	7.90	48.00	9.00	386.00	.20	.34	2.08	.39	16.76
Potassium (K).....	1.10	....	....	3.00	7.00	.03	....	....	.08	.18
Hydrogen (H).....	.00	.08	.00	.00	.00	.00	.08	.00	.00	.00
Sum basic radicles..	....	....	....	....	.....	1.01	1.56	6.25	1.03	19.32
Carbonate (CO_3)...	.00	.00	trace	.00	238.00	.00	.00	.00	.00	7.93
Bicarbonate (HCO_3)	41.00	.00	156.00	39.00	162.00	.67	.00	2.55	.64	2.66
Sulphate (SO_4).....	6.80	76.00	51.00	5.60	145.00	.14	1.58	1.06	.12	3.02
Chlorine (Cl).....	7.00	2.70	97.00	5.80	213.00	.20	.08	2.74	.16	6.00
Nitrate (NO_3).....	.00	1.20	.40	trace	.....	.00	.02	.01	.00	.....
Sum acid radicles...	....	....	....	....	.....	1.01	1.68	6.36	.92	19.61

	A.	B.	C.	D.	E.
1. Soap cost (cents per 1000 gallons)	50	72	211	39	130
2. Pounds, 90 per cent lime to soften 1000 gallons	.35	.11	1.01	.21	2.39
3. Pounds, 95 per cent soda ash to soften 1000 gallons	.05	.57	.75	.00	.00
4. Foaming coefficient, *f*	15	21	130	30	1057
5. Coefficient of corrosion, *c*	−.44	.42	−1.58	−.49	−9.69
C+0.0503 Ca	.11	1.23	1.63	−.08	−8.28
6. Scale, *Sc* (pounds per 1000 gallons)	.59	1.51	1.84	.46	.94
7. Hard scale, *Hs* (pounds per 1000 gallons)	.12	.56	.85	.12	.22
8. Coefficient of scale hardness, *h*	.20	.37	.46	.25	.23
9. Alkali coefficient, *k*	290	440	22	280	2.6

The following boiler classification of the waters (including a verbal and numerical classification) will result from the foregoing figures:

(*A*) (15) Nonfoaming, (−0.44+0.11) semicorrosive, (0.59) very little, (0.20) soft scale.

(*B*) (21) Nonfoaming, (+0.42+1.23) corrosive, (1.51) little, (0.37) medium scale.

(*C*) (130) Semifoaming, (−1.58+1.63) semicorrosive, (1.84) little, (0.46) medium scale.

(*D*) (30) Nonfoaming, (−0.49−0.08) noncorrosive, (0.46) very little, (0.25) soft scale.

(*E*) (1057) Foaming, (−9.69−8.28) noncorrosive, (0.94) very little, (0.23) soft scale.

The effect of suspended matter upon the scale classification of *B* is of interest. Neglecting the suspended matter, the class would be "very little hard scale."

For use in irrigation, *E* would be classed as poor and the others as good.

For detailed comparison or classification of waters, the formulas presented will be found of great value. It is believed that a better general understanding of waters and much practical advantage would result if the the analyst were to devote to the foregoing calculations and the resulting classification a portion of the time usually spent in figuring hypothetical combinations.

For those who desire to use the formulas the following notes are of special interest:

(*a*) The reacting values are necessary only in estimating the error of analyses. Other formulas are presented in dual form so that reacting values may be used or not, as desired. Generally their use will shorten the work of calculation.

(*b*) The formulas are well adapted to the use of a slide rule or similar calculating machine. They are for use primarily in connection with analyses expressed in parts per million or milligrams per liter, but can be used for analyses expressed otherwise if such analyses are reduced to parts per million by multiplying by the proper factors.

(*c*) The numerical coefficients used in the formulas are the result of the simple mathematical calculations of chemistry. Thus the coefficient 0.26 of formula for maximum softening is derived as follows: It is desired to find the quantity of lime (CaO) that will react with certain

substances. The reacting value of this lime must, of course, equal the sum of the reacting values of the substances with which it is to react. The parenthesis of the formula represents this reacting value. The reacting coefficient of CaO being $\frac{1}{28.05}$, our reacting value for lime must be multiplied by 28.05 to give parts per million of CaO. This must in turn be divided by 120 to give pounds per 1,000 gallons. A final division by .90 reduced the expression to terms of lime of 90 per cent purity. Thus $28.05 \times \frac{1}{120} \times \frac{1}{.90} = 0.26$. Other numerical coefficients of the formulas are derived in a similar manner.

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CHAPTER III

FUELS

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Definition. A fuel is a substance whose combustion in atmospheric oxygen can be utilized as a source of heat energy for commercial or domestic purposes.

Classification. Fuels are most conveniently considered as divided into three natural divisions, solid, liquid, and gaseous fuels.

Elementary Constituents. The two elements which contribute most to the heating power of fuel are carbon and hydrogen. Though other elements, such as sulphur, contribute somewhat to the formation of heat, the two mentioned above are by far the most important. That portion of the oxygen which occurs in the fuel as a partial oxidation product of some compound constituent thereof causes a loss in the heating value, as its presence means that a certain amount of the oxidation and heat development have been accomplished outside the furnace. Sulphur in small amounts is usually found in fuels. In large amounts it is undesirable, as it has a corrosive action and renders the fuel unfit for metallurgical uses. Nitrogen is usually an inert constituent, escaping uncombined during combustion. Silicon and phosphorus are also found in fuels, the latter being undesirable in metallurgical work. Together with the last two there is usually a considerable amount of mineral matter which is left after combustion as ash, and usually a certain amount of water which occurs free in the fuel. Ash is undesirable, as it dilutes the combustible matter of the fuel, causes an additional expense for its removal, and may interfere seriously with the use of the fuel because of its low fusion point and the consequent tendency to form clinker. Water is a direct loss of heat, as it dilutes the fuel, requires a large amount of heat for its evaporation, and by escaping up the flue at the temperature of the escaping gases, carries away a certain amount of heat.

Measurement of Temperature. In certain commercial operations it is necessary, in order to secure the best results, that the temperature be regulated between certain limits, and a knowledge of the temperature conditions becomes indispensable. The necessity of careful measurement and systematic regulation of the high temperatures obtained in many commercial operations has been recognized comparatively recently, and

it is well for the student to familiarize himself with methods for measuring high temperatures. The instruments used for this purpose are known as pyrometers.

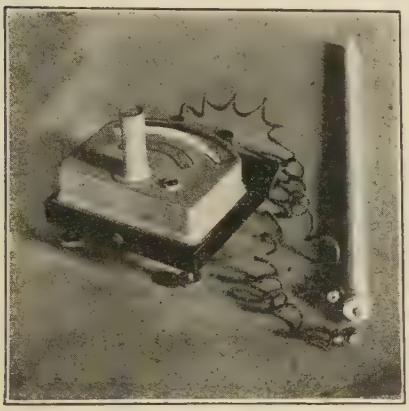

Fig. 62.

Fig. 62 illustrates an instrument known as the Le Chatelier pyrometer. It consists of two wires of dissimilar metals melted together at one end, the other ends being connected with a needle galvanometer of comparatively high resistance. The deflection of the galvanometer needle is dependent on the temperature of the junction, and by providing the galvanometer with a suitable scale, the temperature can be read off directly from the instrument. The wires are generally made, one of platinum, the other of a 10 per cent alloy of platinum and rhodium, though couples of other metals are also used.

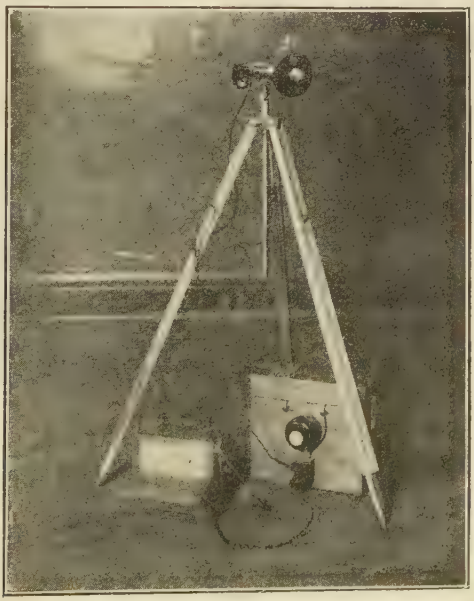

Fig. 63.

Fig. 63 illustrates a form of instrument known as the Wanner pyrometer. It is one of a class known as optical pyrometers, several of which

are on the market. Fig. 64 illustrates the construction of the instrument. Light from a 6-volt incandescent lamp used as a comparison, and from the object whose temperature is sought enters the slits U_1 and U_2, the two beams being rendered parallel by J and each dispersed into a continuous spectrum by R. C separates the dispersed light from both U_1 and U_2, into two beams polarized at right angles. The arrangement of the remain-

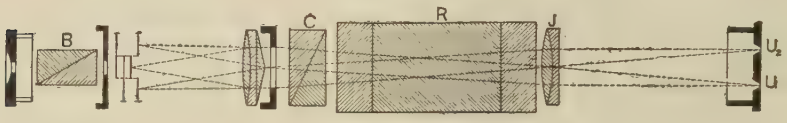

Fig. 64.

ing parts is such as to bring before the analyzer B an illuminated field, half of which is illuminated by red light from the spectrum of U_1, the other half by red light from the spectrum of U_2, the two halves being polarized at right angles to each other. If the analyzer is at an angle of 45° to the plane of polarization of each beam, and U_1 and U_2 are equally illuminated, the field is uniformly bright. If they are unequally illuminated one-half of the field will appear brighter, and they are equalized by turning B, which carries a scale that can be interpreted in terms of degrees of temperature.

Another form of pyrometer, known as the Féry, is also direct reading, and is constructed by focusing the radiations from the object by either a lens or a concave mirror on a delicate thermo-couple.

Such instruments as the optical pyrometers are the only ones which fulfill all requirements for much of the high-temperature measurements to be made in commercial work.

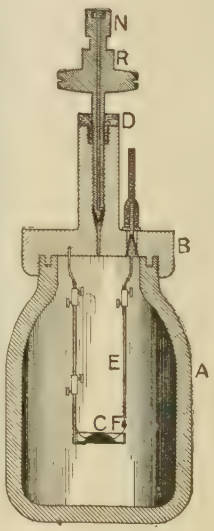

Fig. 65.

Heat of Combustion. The heat of combustion of a substance is the number of calories produced by the complete oxidation of one gram of it. As applied to fuels, it is called the calorific value or heating power of the fuel. The calorific value is one of the most important points to be decided in the purchase of a fuel. Having decided the character of fuel best adapted to the purpose for which the purchase is to be made, the remaining point of chief consideration is the calorific value, which is determined by means of a calorimeter. Solids and non-volatile liquids are usually burned in a heavy steel bomb in an atmosphere of oxygen under a pressure of about 25 atmospheres.

[1] Bulletin No. 2, Bureau of Standards, Washington, D. C.

Fig. 65 illustrates one of the standard forms of this kind of instrument, known as the Mahler calorimeter. It consists of the porcelain or platinum-lined steel bomb A, with a tightly fitting top B, which carries the connection R for admitting oxygen under pressure, the platinum vessel C, into which the substance is weighed, and the terminals for igniting the charge, one of which, E, is insulated from the top B. The substance is ignited by connecting a piece of fine iron wire beween the terminals, having the wire in contact with the charge. When a current is passed through the wire it is heated to incandescence, and both it and the charge are completely oxidized. The calorimeter is immersed in water contained in a vessel protected by non-conducting material from temperature changes. The temperature of the water before and after the experiment, the amount of water and the water equivalent of the calorimeter being known, the total amount of heat liberated by the action is obtained.

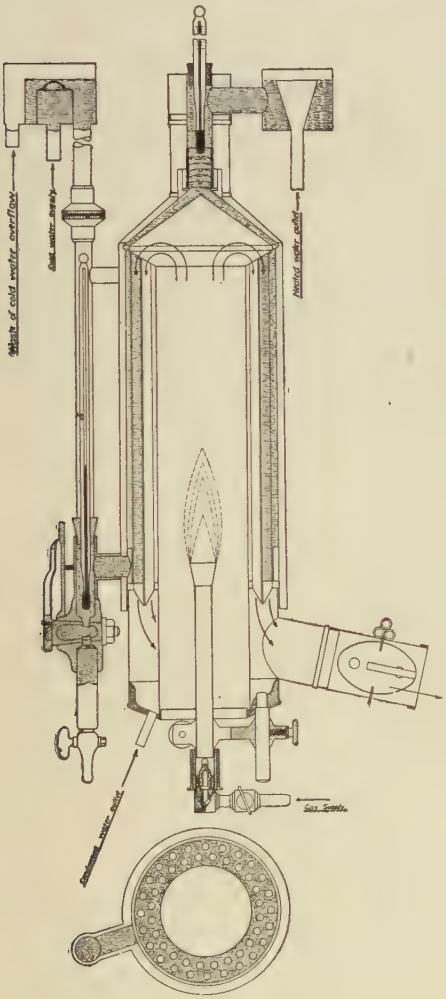

Fig. 66.

The calorific value of gaseous fuels is determined by burning a measured volume of the gas in the atmosphere and determining the amount of heat liberated. Fig. 66 shows a longitudinal and transverse section of a reliable form of gas calorimeter, known as the Junker calorimeter. It is a double-wall copper vessel, so arranged that a steady stream of cold water circulates between the two walls. This stream of water is kept constant by the constant-level devices placed at the entrance to, and the exit from the instrument. The gas, previously measured in an accurate gas meter, is burned in the special burner placed in the combustion chamber of the calorimeter. The heated air and products of combustion ascend to the top of the combustion chamber, and from there descend through two sets of vertical copper tubes which are surrounded by the water that

circulates between the two walls of the instrument. The arrangement of this water jacket and the copper tubes through which the heated gases pass is best seen from the horizontal cross-section of the calorimeter shown below in Fig. 66. During the passage of the heated gases through the water-cooled tubes the heat is taken up by the water and the temperature of the water in its passage through the instrument is somewhat increased. Before beginning a determination the flow of water is started through the instrument, the burner lighted and the thermometer readings allowed to become steady. In this way the water passing through the calorimeter during the burning of a known volume of gas contains all the heat resulting from the combustion of this gas. This water is collected and weighed, the increase in temperature of the water is obtained by the difference in the readings of the two thermometers, and knowing the volume of gas burned from the readings of the meter, all the data have been obtained for calculating the heating power of the gas per unit volume.

The heating power of the gas can be calculated from the chemical composition and heats of combustion of its constituents. But the time required to obtain an accurate analysis is greater than that required by the above determination, and it offers no advantages over the direct determination.

Solid Fuels

Wood. Wood is composed principally of cellulose and ligno-cellulose in about equal quantities, together with gums, resins, a variable amount of water, and inorganic matter left as ash when the wood burns. Cellulose has the composition $(C_6H_{10}O_5)_x$ and is the principal constituent of the cell membranes of young plants. The formula above serves only to give the percentage of the constituents, the molecule being very complex.

Ligno-cellulose is the substance with which the cellulose of young plants becomes incrusted as it grows old, and becomes woody fiber. It is not a carbohydrate, and little is known of its chemical nature.

Wood has a low calorific value, varying from 3000 to 3500 calories, and contains a considerable amount of moisture, the amount depending on the kind of wood, the season in which it is cut, and the extent it has been allowed to dry, being rarely less than 18 per cent.

Wood is of little value as a fuel, as it has a low calorific value, and is too expensive. But it is sometimes used on account of its cleanliness and small amount of ash formed.

Below is given a table [1] containing the results of the analysis of seven different kinds of wood together with their calorific values:

[1] Jour. Chem. Soc., Vol. XLVI, p. 477 (1884).

	C	H_2	N_2	O_2	Ash	Calories
Oak	50.16	6.02	0.09	43.36	0.37	4620
Ash	49.18	6.27	0.07	43.91	0.57	4711
Elm	48.99	6.20	0.06	44.25	0.50	4728
Beech	49.06	6.11	0.09	44.17	0.57	4774
Birch	48.88	6.06	0.10	44.67	0.29	4771
Fir	50.36	5.92	0.05	43.39	0.28	5035
Pine	50.31	6.20	6.04	43.08	0.37	5085

Peat. There is no doubt that peat represents a comparatively early stage in the transformation which vegetable matter undergoes when sufficiently protected to prevent its complete oxidation, as in many localities it is possible to observe the transition from the vegetable matter covering the ground to the underlying peat in various stages of formation. In the upper portions the vegetable matter is easily discernible, while at the bottom, most, if not all, visible signs of plant remains disappear. The formation of peat occurs in bogs or swamps where sufficient vegetable matter accumulates to give rise to the formation. The deposit from each year's growth, such as mosses, grasses, leaves, branches and trunks of trees fall and are partially protected by the water from complete decomposition. The action of organisms and atmospheric oxygen transforms this material first into a loose brown substance, finally, with the aid of pressure from above, into a brown or black peat.

Little is known of the chemical compounds composing peat. Some solvents and solutions of alkalies dissolve considerable amounts of organic matter of a complex character from peat, but the substances obtained from these solutions are probably impure.

Peat has long been used as a fuel, and in northern and western Europe, and in Ireland (where peat bogs are said to cover one-tenth of the total area) it has been extensively used. Peat bogs are also widely distributed in this country and Canada.

The recent peats are usually brown in color and approach wood in chemical composition, containing less oxygen and hydrogen and more carbon. The oldest peats are usually dark in color, and the percentage of carbon is greater than in recently formed peats.

Peat has a higher calorific value than wood, varying from 3500 to 5000 calories. As it is cut from the ground it contains a large amount of water, often as much as 90 per cent of its weight. If the blocks are left to dry under cover in the air this is greatly reduced. The difficulty of freeing it from this water is one of the drawbacks to its use. By application of pressure much of it can be expelled, but it still contains a considerable amount on account of its jelly-like character. A recent observation [1] that this jelly-like character is destroyed by heating it to 150° after which

[1] Engineering, 87, p. 737.

the water can be expelled by pressure, may assist in the solution of this difficulty.

The following analyses[1] give an idea of its composition and the progressive increase in carbon and loss of oxygen taking place during the peat formation:

	1	2	3	4	5	6	7
C	49.88	50.33	50.86	59.71	59.70	59.71	62.54
H	6.54	5.99	5.80	5.27	5.70	5.27	6.81
O	42.42	42.63	42.57	32.07	33.04	32.07	29.24
N	1.16	1.05	0.77	2.95	1.56	2.95	1.41
	100.00	100.00	100.00	100.00	100.00	100.00	100.00

1. Sphagnum, the chief peat-forming plant.
2. Light peat near surface.
3. Light peat.
4. Moderately light peat.
5. Black peat.
6. Black peat.
7. Heavy brown peat.

Peat is frequently formed into briquettes, when it makes an excellent fuel for domestic uses, as it burns with a bright cheerful flame and without much smoke. The following table gives the analyses of samples of peat from this country.

ANALYSES OF PEAT (AIR DRIED)

Locality	Florida	Michigan	New York	
Moisture	10.17	14.22	7.09	
Volatile Matter	54.93	49.11	56.09	
Fixed Carbon	28.98	24.83	24.83	23.97
Ash	5.92	11.84	12.85	
Calories	5249	3979	4275	

Lignite. Lignite or brown coal are names applied to the substances which represent the next stage to peat in the transformation of vegetable matter into coal. The distinction of lignite from peat on the one side and bituminous coal on the other is not sharp, as the transition from one to the other is gradual. Chemically, lignite seems to be more closely related to peat than to bituminous coal and, as with peat, it is found that certain solvents and solutions of alkalies dissolve considerable organic matter of a complex character from lignites. The evidences of vegetable origin are not usually distinct in lignites, though when properly treated, microscopic examination is usually able to show the remains of plant structure. In general, lignite is denser, darker in color, and contains more carbon than peat. It contains about 35 per cent of water, and on air-drying this falls to about 15 per cent. Its calorific value varies

[1] Jour. Prakt. Chem., vol. 92, p. 65.

from 4000 to 6500 calories. The amount of ash varies greatly, but should not exceed 10 to 15 per cent.

On account of the difficulties encountered in shipping and storing lignite, its formation into briquettes has been practiced to a considerable extent, especially in Germany. In this country the necessity for using such fuels has not been greatly felt, and the operation of briquetting such fuel is here in its beginning. This question will be mentioned later in connection with bituminous coal.

The following table gives the analysis of some samples of lignite from this country:

Locality	N. Dakota	Texas	California	Wyoming	Montana
Moisture.....	16.70	22.48	18.51	17.69	9.05
Volatile Matter...	37.10	31.36	35.33	37.96	36.70
Fixed Carbon.....	39.49	26.73	30.67	39.56	43.03
Ash.....	6.71	19.43	15.49	4.79	11.22

Bituminous Coal. The next stage in the formation of coal is represented by bituminous coal, by far the most important of all the classes of fuels. The division of bituminous coals from lignites is more sharply defined than that of lignites from peats, but still the transition is gradual.

The origin of coal is swamp flora laid down when the growth of vegetable matter was far more luxuriant than now, and which in earlier geologic ages has passed through successive stages which are represented now by peat bogs and beds of lignite.

The properties of bituminous coals differ widely. The amount of volatile matter varies from 15 to 50 per cent, the amount of ash from 2 to 20 per cent, but the most marked differences are observed in the coal substance when heated. The differences are noticed in the characters of both the volatile matter and the residue or coke. Some, when heated, fuse together to a compact mass, and if heated sufficiently leave behind a firm, solid mass composed principally of carbon and the ash of the coal. Such coals are said to be caking coals. Non-caking coals do not fuse and the mass left behind when such coals are heated coheres only slightly or not at all.

Coals are frequently changed, after mining, by the absorption of oxygen and the loss of some of their combustible constituents, and on long standing their heating power is materially changed, some, even losing their caking power. Frequently, this absorption of oxygen is so rapid and accompanied with the evolution of so much heat that when large amounts are stored in one pile the temperature gradually rises until spontaneous combustion ensues.

To overcome some of these difficulties and to utilize those portions of the fuel which unavoidably go to waste around the mine, finely divided

coal is frequently mixed with pitch or tar, and compressed while hot into molds. These briquettes are less bulky, less likely to deteriorate and to undergo spontaneous combustion, and can be fired more efficiently than the raw coal. Where it is necessary to keep large stores of coal on hand, these advantages are sufficient to justify the operation of briquetting. The practice of briquetting coal and lignite is more common in Germany than in this country. In 1906, 14,500,851 tons of briquettes were made in Germany, including those made from lignites.

One of the chief objections to the burning of bituminous coals is the production of smoke during combustion. It is doubtful if this can be prevented by any means which involves the introduction of fresh coal directly into the fire. Mechanical stokers, such as illustrated in Figs. 67 and 68, are designed to bring the fuel into the fire slowly, and at a regular rate. In Fig. 67, this is accomplished by a rocking motion of the grate bars

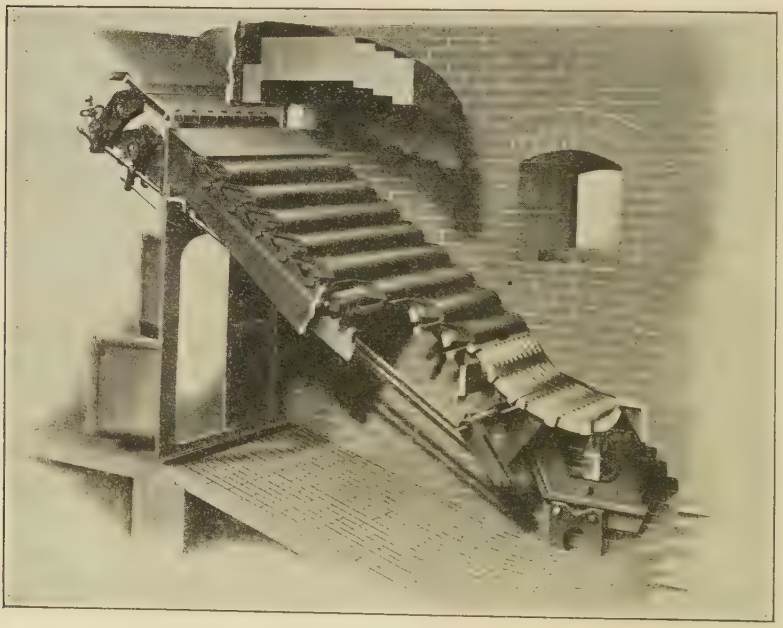

Fig. 67.

which are set at the proper angle, and in Fig. 68 by the forward motion of the grate bars arranged as a continuous chain. In this way the volatile matter is expelled gradually and mixed with sufficient oxygen for its combustion, the result being that less smoke is produced, the fire kept in a more uniform condition than is possible by hand firing, and at the same time the fuel is consumed more efficiently.

	Moisture.	Volatile Combustible.	Fixed Carbon.	Ash.	Sulphur.	Calories.
West Virginia	0.80	32.24	62.33	4.63	1.65	8167
Indiana	4.93	35.28	50.82	8.97	1.00	6979
New Mexico	1.36	33.77	52.31	12.56	1.21	7173
Kentucky	1 16	30.81	61.01	7.02	0.58	7785
West Virginia	0.47	14.80	81.59	3.14	0.52	8447
West Virginia	0.60	15.48	79.64	4.28	0.46	8306
Illinois	4.00	28.86	58.56	8.58	0.95	7056
Illinois	7.67	28.96	57.69	5.68	0.48	6958
Pennsylvania	1.47	27.63	63.66	7.24	0.97	7875
Pennsylvania	0.71	16.59	76.83	5.87	0.98	8296

Analyses made in the fuel-testing laboratory of the Technologic Branch, U. S. Geological Survey.

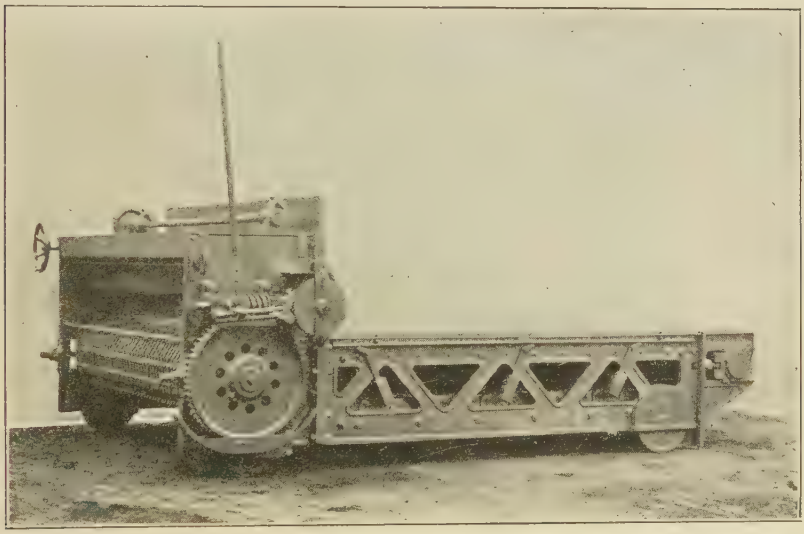

FIG. 68.

Anthracite. In composition the anthracite coals approximate the final stage in the carbonization of vegetable matter. On one side of the anthracite we have bituminous coals separated by the semi-anthracites, and on the other side the anthracites approach graphite. As indicated above, anthracites contain a large amount of fixed carbon as compared with their content of volatile matter. They are denser than bituminous coals, have a conchoidal fracture and a high kindling temperature. Anthracite is used largely for metallurgical work, for the manufacture of producer and water gases, and for domestic purposes. As it has little volatile matter, and burns with a non-luminous flame, it is well adapted to these purposes.

Below are the analyses [1] of some semi-anthracite and anthracite coals of this country:

Locality	Arkansas	Rhode Island	Indian Ter.	Virginia	Pennsylvania
Moisture	5.19	2.41	5.11	4.80	3.33
Volatile Matter	10.49	4.92	13.65	10.12	3.27
Fixed Carbon	70.31	73.61	73.21	67.05	84.28
Ash	14.01	19.06	8.03	18.03	9.13
Sulphur	2.05	0.07	1.18	0.63	
Calorific Value	6922	6109	7590	6645	7417

Charcoal. Charcoal is made from wood by two methods. By the first, wood is converted into charcoal by what is called the charring process. This consists of piling the wood into large circular heaps, leaving horizontal flues near the bottom and a vertical flue at the center for the escape of the evolved gases and covering over the whole, except for these points of ventilation, with powdered charcoal, earth and turf. At the points of ventilation the wood burns, the area of the combustion depending on the drafts, and the heat produced by the burning at these points suffices to raise the temperature of the whole mass to the point where most of the volatile matter of the wood is expelled. When all the volatile matter has been driven off and the escaping gases cease to burn with a luminous flame, the draft holes are covered and the operation stopped. By this process air-dried wood yields about 25 per cent of charcoal, but all the volatile matter is lost.

By the second method of preparing charcoal provision is made for the recovery of these by-products, which consist of combustible gases, wood alcohol, organic acids, acetone and tar. For the details of this process see Chapter XXII. The operation consists in the destructive distillation of wood from closed vessels, the charcoal remaining in the retort. For the production of charcoal for certain purposes these retorts are heated by means of super-heated steam.

Charcoal is quite porous and brittle and retains the shape of the wood, though the pieces are only about three-fourths the size of that of the wood. It still contains traces of volatile matter from which it is impossible to free it, and the ash-forming constituents of the wood. It burns with little flame, contains little sulphur and phosphorus, a low amount of ash, and has been extensively used in metallurgical work, especially for the production of the finer grades of iron and steel. Its calorific value is about 7000 calories. The porosity depends on the character of the wood used in preparing it, some giving a denser product than others. It possesses the peculiar property of condensing many gases before they reach their point of liquefaction, and of abstracting coloring matter from

[1] Analyses made by U. S. Bureau of Mines.

solutions. This power of absorbing materials is frequently utilized to purify solutions from tarry materials and coloring matter. Because of the great tendency of charcoal to hold back small amounts of other substances perfectly pure amorphous carbon is unknown.

Coke. Coke is the residue left after the destructive distillation of coal, and is composed principally of carbon and the ash-forming constituents of the coal from which it was formed.

The production of coke was at first carried out in much the same way that charcoal is obtained from wood in charcoal kilns; the bee-hive oven of to-day, in which most of the coke produced in this country is made, is a development of this method.

Fig. 69 illustrates the bee-hive oven as used in this country. It is simply a dome-shaped enclosure built of fire brick, 12 ft. in diameter, 7 ft. high, with an opening at the top for charging and for the escape of the products of combustion and volatile matter formed during the opera-

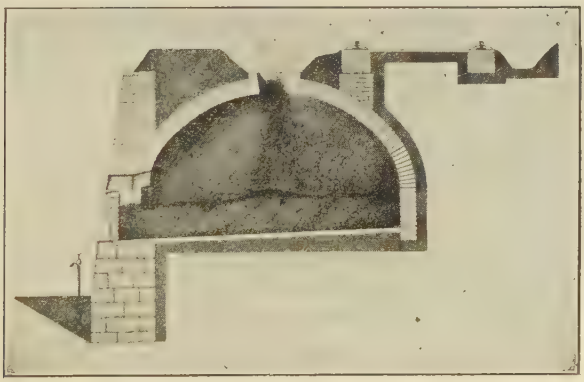

Fig. 69.

tion, and a door at the side through which the coke is withdrawn, usually by hand, at the end of the operation. This door is built up with fire-bricks during the process, except at its top above the level of the charge. In this way five to six tons of coal are coked at each charge, and the time required from forty-eight to seventy-two hours, yielding from 60 to 65 per cent of coke. The operation is brought to an end by quenching the fire in the oven with a stream of water, after which the coke is withdrawn. These ovens are usually built together in one or two rows, with a track on top to bring up the coal.

As seen from the above description, the burning of a part of the coal furnishes the heat necessary for coking the remainder, and the volatile matter of the coal is either burned or turned into the air.

Numerous forms of ovens have been designed to collect these products and use them. These so-called by-products consist of combustible gases,

various organic compounds, compounds of nitrogen including ammonia and tar.

Figs. 70, 71 and 72 are illustrations of two types of by-product coke

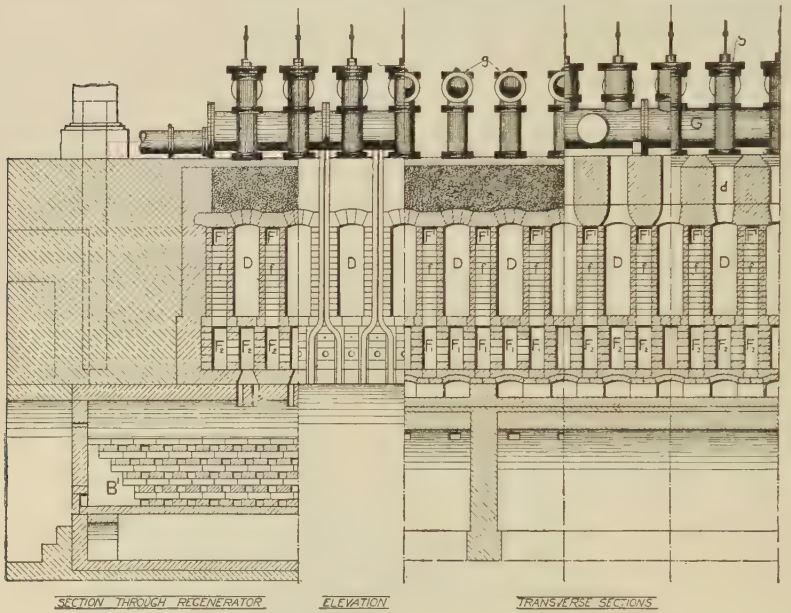

FIG. 70.

ovens which are used considerably in this country and will serve to illustrate the operation.

The Otto-Hoffmann type of oven is shown in transverse and longi-

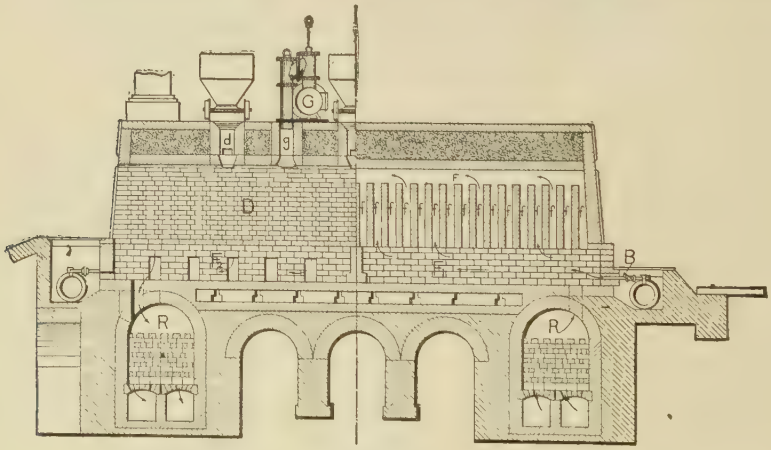

FIG 71.

tudinal sections in Figs. 70 and 71. The coal is charged through *d* into the coking chambers *D* beneath. These are long, narrow retorts of fire-

brick construction placed side by side, usually in groups of fifty. In the walls separating the retorts are the vertical flues f, in which the gas evolved in coking previous charges is returned from the condensing house and burned to furnish the heat for coking the charge. The retorts are about 33 ft. long, 6½ ft. high and 20 ins. wide, closed at each end by an iron door which is raised and lowered electrically, and during the coking process luted with fire-clay. The air for the combustion of the gas passes through the checker work R, made of refractory material, which, as we will see, is highly heated, the gas entering at the burner B. The burning gases pass along the horizontal flue F_1, and up each of the vertical flues f of one-half of the retort wall to the upper horizontal flue F^1, then down the remaining vertical flues f of the second half of the wall to a similar horizontal flue F_2, situated beneath the coking chamber D, then out through the second chamber or regenerator R' filled with refractory checker work, where the heat of the escaping gases is abstracted by heating up the checker work to incandescence. After a certain length of time, when R' has been heated and R cooled, the currents of air and gas are reversed through the flues, the air entering through R' and the gas through another burner at the other end of the retort. The volatile products escape from D through the uptake pipes, provided with valves, and pass into the common main G at a high temperature, and are gradually cooled in the iron pipes, depositing some of the condensable portions, the remainder being subsequently removed in the condensing house.

After the completion of the coking process, the charge is removed by a steam or electrically operated pusher, which pushes the whole charge of the retort out on the opposite side, where it is rapidly cooled by a stream of water.

The time required for coking a charge in this type of oven is about twenty-four hours, yielding about 70 per cent of coke.

In the Semet-Solvay type of by-product oven, shown in Fig. 72, the coking chamber D is somewhat similar to that of the Otto-Hoffmann oven above. They are built in sets of thirty or forty, are 35 ft. long, 7½ ft. high and 16½ ins. wide.

The coal is charged through d into the coking chamber D, the volatile products escaping through g into the common main G. The flues f, built in the walls of the ovens, are in this type five in number and arranged horizontally. The gas returned from the condensing house is delivered at the four burners B, and mixes with preheated air delivered from beneath the oven. The current of burning gases is from the top flue downward through each of the others, fresh gas burning at each of the burners during their downward course. The gases from the flues in each wall of the chamber pass into a single flue beneath D, thence into a series of channels with thin walls where the air passing to the burners is preheated, as stated above. The flue gases are subsequently passed through water-tube boilers, and their remaining heat used to generate steam for power

purposes. A charge of from seven to nine tons of coal can be coked in these ovens in about twenty-four hours.

Coke is also obtained as a by-product in the manufacture of coal gas, which will be mentioned later. But the coke obtained in this way is soft and unfit for metallurgical purposes, and is partly consumed in the producer used to heat the retorts, and for domestic purposes.

During the coking process the coal fuses and the escape of the gases formed by the destructive distillation of the coal leaves the residue or coke full of cavities, the walls of which are quite hard. This cellular structure is very advantageous, as the coke to be of service for metallurgical work must be sufficiently strong to sustain the charge above without crushing, and at the same time must be porous. It has a silvery

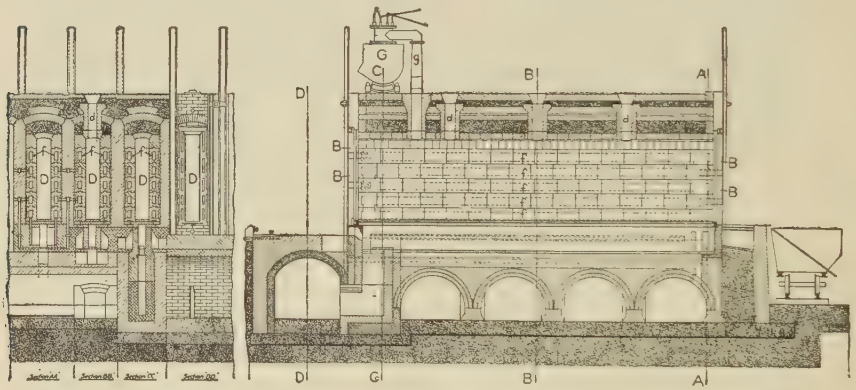

FIG. 72.

white luster, a metallic ring when struck and is infusible. It burns without smoke and has a calorific value of 7600 to 8100 calories. All of the ash of the coal and ordinarily about half of the sulphur remain in the coke, and it is frequently necessary to wash the coal to remove portions of these constituents in order to make a serviceable quality of coke. The phosphorus of the coal is all found in the coke. Besides these, there is a considerable amount of nitrogen and water, and small amounts of hydrogen and oxygen which cannot be driven off by heat. Some coals, which do not yield a good quality of coke, can be mixed to advantage with a good coking coal.

The chief use of coke is for metallurgical purposes, but a great deal is used in gas producers, on railroad engines and for domestic purposes.

The objection to the use of coke made in by-product ovens seems to have been without foundation, and the relative amount of coke made in the by-product ovens has increased steadily and rapidly. About 16.5 per cent of the coke made in this country is made in the by-product ovens, and in Europe these ovens are in general use. It seems that in a short time most of the coke made in this country will be made in this way, the increase being limited only by the demand for the by-products.

Liquid Fuels. The only liquid substances which have any extended use as fuels are crude petroleum and various products obtained by its fractional distillation; as petroleum spirit, lamp oil, and the residue or "residuum" left in the retort after the distillation of the lubricating oils. Tars obtained as by-products in other industries are sometimes burned as fuels when a more remunerative market is not available, but they are too expensive for this purpose. The objection of expensiveness applies also to alcohol at present, but as it possesses certain advantages as a fuel, and its production is subject to our control, it is possible that it may assume more importance in the future if it can be produced more cheaply.

Petroleum. Petroleum is widely distributed, but 86 per cent of the world's output comes from this country and Russia; the United States producing 63 per cent and Russia 23 per cent of the total.[1] In this country the Pennsylvania fields have been most prominent, and it was here that oil was first obtained by systematic borings. Besides Pennsylvania, many other states have become oil producing states, as Ohio, Texas, and California.

In using crude petroleum as a fuel the greatest objection is that the volatile portions will escape and mix with air and form an explosive mixture, as it requires only small amounts to form an explosive mixture with air. But it is only necessary to remove these by distillation to avoid such danger.

In burning crude oil in furnaces it is first converted into a very fine spray by means of special burners, and the spray directed against refractory material, which, becoming incandescent, transmits much heat to the boiler by radiation, and it also effects better combustion. These burners are operated in two ways. In the first, the oil is "atomized" by forcing it under pressure through burners so constructed as to send the oil into the furnace in a sheet of finest spray. By the second the same disintegration of the oil is accomplished by a jet of steam. The objection to the second method is that a large amount of steam is consumed, and the flame is cooled down at the point where the combustion should be most rapid, and, while steam is effective in securing the combustion of the last portions and preventing the formation of smoke, it can be best introduced later in the flame and in smaller amounts.

Several advantages are obtained by using petroleum as a fuel. It has a high calorific value, from 10,000 to 10,500 calories, is more uniform than coal, is easily regulated to secure complete combustion and the rate of combustion can be changed by merely turning the valve admitting the fuel. It does not deteriorate if kept in covered tanks, and no spontaneous combustion occurs. It requires a small fraction of the number of stokers required to burn coal, gives no ashes, cinders or smoke when properly burned, and is easily transferred at sea through flexible hose by pumps.

[1] The Production of Petroleum in 1907. U. S. Geological Survey.

Still the output is so small when the total amount of fuel consumed is considered, and the supply so uncertain, that it seems that petroleum as a fuel must remain an adjunct except near the sources of supply and for certain special purposes such as on fast ocean-going ships, for use in navies, and to assist in meeting sudden demands on powerhouses of a temporary character.

Gaseous Fuels. When the products of combustion of solid fuel are allowed to pass through a bed of incandescent carbon they are partially reduced, and can be ignited on their escape. The pale blue flame often seen burning at the top of an open grate fire is an illustration. And if the fuel bed were sufficiently thick and hot enough to reduce most of the carbon dioxide and water formed at the bottom of the grate, and provision made for collecting the gas, we should have a sample of producer gas.

Producer gas is, then, the combustible gas obtained by the burning of solid fuel with a restricted supply of air, or with air and steam together in such a way that there is subsequent reduction of the products of combustion and the steam by incandescent carbon. When air alone is used, the gas is called "air gas." When steam is blown in along with the air the gas obtained is called "semi-water gas." By the action of steam alone on heated carbon the product is "water gas."

Whenever carbon burns the first product of the reaction is carbon dioxide according to Eq. (1) $C+2O=CO_2+96960$ calories. If the supply of oxygen is limited and there is sufficient contact of the gases with the carbon the temperature increases until the carbon dioxide first formed is partially reduced according to Eq. (2) $CO_2+C=2CO-38960$ calories. Of the 96960 calories developed in the formation of the gram-molecule of carbon dioxide according to Eq. (1), 38960 calories are consumed in the second reaction and stored up as chemical energy in the carbon monoxide formed, and 58,000 calories liberated. As two gram-molecules of carbon monoxide are formed in Eq. (2), the 58,000 calories liberated constitute about 30 per cent of the total heat of combustion of the two gram-molecules of carbon which are present in the combustible gas formed, when burned according to Eq. (1). In other words, by this method of converting solid carbon into carbon monoxide, about 30 per cent of the heat of combustion of the carbon is liberated in the producer, even if the reaction according to Eq. (2) is complete, which is never the case, for the reaction is, as represented, reversible, and for every temperature there is a definite composition of the gas mixture which is in equilibrium with carbon at that temperature. The extent to which the action approaches equilibrium depends on the velocity of the action and the time and extent of contact of the gases with the heated carbon. This heat evolved in the producer need not all be lost, as the gases may be used while much of this heat is contained in them, or it may be used to preheat the air and steam put into the producer, but the loss will still be about 20 per cent of the heat of combustion of the carbon.

Producer gas has the lowest calorific value of any gaseous fuel, and the temperature of its flame is the lowest of any, yet it is the cheapest artificial gas per unit of heat. It has become of great commercial advantage, as nearly any kind of solid fuel can be converted into a gaseous fuel in the producer. Although about 20 per cent of the total heat of combustion of the fuel is lost in the producer, the remainder can be used so efficiently that the loss is more than retrieved. Its use in connection with the gas engine is an efficient means of power generation. With care it can be burned with a small excess of air, and complete combustion secured, causing a smaller amount of heat to be carried away by the escaping gases.

It is finding application in commercial work of many kinds where a gas of high calorific value is not required.

Siemens' Regenerative Furnace. The method used in connection with the Otto-Hoffmann oven above, for recovering the heat from the flue gases is known as the regenerative system. Fig. 73 is an illustration of this type of furnace, which was first worked out by Siemens in connection with his gas producer, and known as the Siemens "regenerative" furnace. Beneath the furnace proper, *A*, are four chambers, *B*, *C*, *D*, and *E*, filled loosely with firebrick. The gas and air enter through *B* and *C*, and after burning pass out through *D* and *E*. After the interior of *D* and *E* is highly heated the direction of the gases is reversed, the gas and air entering through *D* and *E*, where they are highly heated before burning, and escape through *A* and *B*. Various methods have been worked out for the recovery of the heat contained in the gases which escape after the completion of an operation. This is illustrated in the Otto-Hoffmann and Semet-Solvay coke ovens above, and in connection with gas producers it is a matter of considerable importance to use as much as possible of the heat of the escaping gases to preheat the air and steam introduced into the producer.

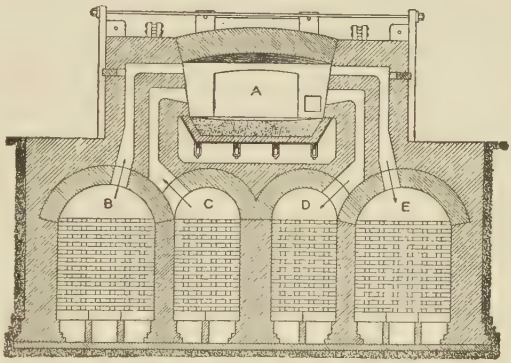

FIG. 73.

Combustion. It is not possible to discuss here the problem of combustion in a theoretical way, and the student must be referred to some of the larger works where this subject is discussed. It may be said in a general way that the object sought in the combustion of fuel is to secure complete combustion of the fuel with as small an excess of air as practicable. There are many factors which are involved in obtaining

these results, one of the most important of which is to obtain a thorough mixing of the air with the volatile matter produced from the heated fuel. An occasional analysis of the flue gases is a necessary guide for the proper management of the furnace, and there are instruments now on the market for the automatic recording of the content of carbon dioxide in the flue gases which are very helpful in the management of the furnace. Gaseous fuel can be burned with very little excess of air by conducting a mixture of air and the gas through or over porous material such as porous fire clay.[1] Of course care must be taken to prevent back-firing of the mixture.

Water Gas. Steam is usually forced into the gas producer along with air to overcome practical difficulties encountered in operating the producer with air alone, and at the same time to increase the calorific value of the gas. As the action of steam on carbon is accompanied with an absorption of heat, it is necessary to supply heat to continue the operation. The production of "semi-water gas" is made a continuous operation by the heat generated by the action of the oxygen of the air on the fuel in the producer. By separating the two operations taking place in the formation of "semi-water gas," and collecting the resulting gases separately, we would obtain "air gas" and "water gas." The intermittent operation of the producer with air and steam is the usual method of preparing water gas. The producer is operated a few minutes with air until the temperature is sufficiently high, when steam is passed in until the temperature falls too low to produce a gas of high calorific value.

The action of steam on highly heated carbon results in the formation of carbon dioxide, hydrogen, and carbon monoxide in proportions varying with conditions. It is customary to express the action by the following two equations:

$$(1) \quad 2H_2O + C = CO_2 + 2H_2 - 18340.$$
$$(2) \quad H_2O + C = CO + H_2 - 28650.$$

At low temperatures the reaction is mostly according to Eq. (1) while at more elevated temperatures, according to Eq. (2).

As the gases formed by these two reactions are capable of reacting according to Eq. (3) $CO_2 + 2H = CO + H_2O - 9310$, and since equilibrium is obtained more readily between gases than between a solid and a gas, the composition of the water gas will tend to approach the condition of equilibrium according to this equation.

The producer used to generate water gas does not differ greatly from the ordinary gas producer. The first successful water gas plant was worked out by Lowe in 1874.

For illuminating purposes, water gas which burns with a non-luminous flame is passed over highly heated surfaces over which a slow stream of petroleum is allowed to flow. The products of decomposition

[1] Engineering, p. 91-487.

of the petroleum mixing with "water gas" contribute the desired illuminants. (See Chapter XX.)

By having a thin fuel bed it is possible to operate during the introduction of air in such a way that practically no carbon monoxide is produced, and the total heat of combustion of the carbon consumed is liberated in the producer. The time required for the operation with the air blast is much reduced in this way. The composition of water gas is about as follows:

Hydrogen	51.5
Carbon monoxide	41.0
Methane	0.1
Carbon dioxide	4.0
Nitrogen	3.4
	100.0

It is composed almost entirely of combustible gases and has a calorific value much higher than producer gas. The presence of such large amounts of carbon monoxide, which is highly poisonous and without odor, constitutes a danger in its use.

Coal Gas. Coal gas is made by the destructive distillation of coal in fireclay retorts of special construction. They are mounted above a gas producer which furnishes the gas with which the retorts are heated. Above is a fireclay arch. Each retort effects the distillation of a charge of about 400 lbs. in four hours. The gas escapes through a cast-iron mouthpiece which closes the open end of the retort and into a common main, where the opening of each tube is water sealed to prevent back pressure when the retort is opened.

The composition of the gas varies with the kind of coal used and the conditions during distillation. These cause greater change in the illuminating power than in the calorific value. It burns with a bright, often sooty flame, and as it is composed almost entirely of combustible gases it has a high calorific value. The coke left in the retort is of inferior quality because of the method used to effect distillation and the character of the coal necessary to form a good quality of gas.

It is used principally for illuminating purposes, and on account of its high calorific value, it is used to some extent where a great deal of fuel is not needed. For further particulars see Chapter XX.

The following [1] is an average composition of coal gas:

Hydrogen	48.0
Carbon monoxide	8.0
Methane	36.0
Unsaturated hydrocarbons	3.8
Nitrogen	4.2

[1] J. S. C. I., 1888, p. 20.

Oil Gas. Oil gas is made by the destructive distillation of petroleums. It is somewhat similar to coal gas, and contains a considerable amount of unsaturated hydrocarbons which imparts luminosity to the flame.

Natural Gas. Natural gas occurs ready, formed in the earth, and in the oil regions of Pennslyvania and Russia it is found in enormous quantities. It always accompanies petroleum, and their origins are closely connected. It is frequently confined under great pressure, and when borings are made through the overlying strata its escape is at times beyond control. While it always accompanies petroleum, it is sometimes found alone.

As it is composed almost entirely of combustible gases, its calorific value is very high. The natural gas of this country burns with a slightly luminous flame, and has a higher kindling point than other gaseous fuels. When it is properly burned it is an excellent fuel because of its high calorific value and practically smokeless flame.

The composition of natural gas varies according to the locality, that from any one district remaining quite uniform in composition.

Gasoline. During recent years large quantities of the low boiling fractions of petroleum have been used in internal combustion engines. These low-boiling fractions, known as gasoline, are now used in such enormous quantities that efforts have been made to increase the output above that obtained by simply distilling off the low-boiling fractions of petroleum. Gasoline is now also obtained from natural gas supplies by condensing the vapors of *liquid hydrocarbons* contained in the combustible gases. The most important recent development in the production of gasoline is its formation from the higher-boiling fractions of petroleum. This is accomplished by the decomposition of the more complex molecules of the higher-boiling fractions of petroleum into low-boiling fractions of smaller molecular weight. This process is known as *cracking.* A number of such processes have been devised and several have been put into operation. *Aluminum chloride* is sometimes used in this operation. The most widely known of these operations is the *Burton process.*

The *Burton process* is a method for making gasoline from high-boiling hydrocarbons and was worked out in the laboratory of the Standard Oil Company of Indiana. It has been in commercial operation since 1913, and has been the most successful of the various processes proposed for making gasoline from heavier oils. There are in operation now, at different plants throughout the country, 967 stills, which produce daily about $1\frac{1}{4}$ million gallons of gasoline.

The material that is transformed by this process is an intermediate distillate from petroleum. It is the fraction coming off after the lighter fractions of gasoline and kerosene and before the fractions suitable for lubricating oils. This fraction is commonly known as fuel or gas oil, and most of it boils above 260° C.

The process consists in the distillation of this heavy oil under a pressure of 4 or 5 atmospheres. This pressure is obtained and maintained

during the distillation by gas, which is formed by decomposition of the oil.

The gasoline made by this process is practically the same as gasoline made by simple distillation of crude oil. It contains more unsaturated hydrocarbons. But for use as a fuel in internal combustion engines, it is as good as the gasoline from the crude oil.

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CHAPTER IV

SULPHURIC ACID

WILLIAM M. GROSVENOR

Occurrence. Sulphuric acid is found in commerce as: Chamber acid (about 53° Bé., 66.6 per cent H_2SO_4) taken from the bottoms of the chambers in the chamber process; Glover acid (about 60° Bé., 77.7 per cent) taken from the first or Glover tower of the chamber process; 66 acid, is fairly pure acid concentrated (see p. 130) to 66° Bé., 93.2 per cent; 98 acid, of 98 per cent, made by concentration or by the contact process (see p. 147) and generally of great purity; oleum or fuming acid (100 per cent H_2SO_4 containing additional SO_3 in solution), made by distillation of sulphates (obsolete) or by the contact process; Nordhausen acid (oleum when made from distillation of weathered shales [obsolete, containing iron sulphate or from $FeSO_4$), approximating a composition $H_2SO_4SO_3$ or $H_2S_2O_7$ which is pyrosulphuric acid; and oil of vitriol, also called o.v. (generally about 66°). The old name, "oil of vitriol," is derived from its first preparation by the alchemists Gaber, Valentine and their predecessors, who made it by distillation of sulphates, particularly green vitriol, $FeSO_4$, or by the burning of sulphur after the addition of saltpeter. In fact, historically, sulphuric acid is one of the first isolated acids, known to the Arabians in the eighth century and to Europe in the fourteenth and fifteenth centuries, when chemical industries really began to develop.

Industrial Position. The importance of an industry is something by which we should always be guided. The tonnage indicates to a great degree the opportunity for engineering skill; the value marks the utility of effort to improve (except revolutionary improvements that establish entirely new price levels and thereby new horizons of usefulness). There are something over 1 0 sulphuric acid plants[1] in the United States, the majority of the plants being located in Georgia, Pennsylvania, New Jersey, New York, South Carolina, Maryland and Ohio. Expressed in short tons and calculated as 50° Bé), the production of sulphuric acid in 183 works in the United States was 2,748,527 tons in 1909. These works are distributed approximately as follows: North Atlantic States,

[1] In 1916 we find that 211 plants produced 5,642,112 tons, worth $62,707,369, and 443,332 tons over 66° and therefore not included by the U. S. Geol. Bureau in the acid figured to 50° Bé. Note the wonderful increase.

41 per cent, South Atlantic, 29 per cent, North Central, 18 per cent, South Central, 8 per cent, and the Western, where mining and agriculture predominate, 4 per cent. One would, therefore, not consider a very large installation in the West without providing some new outlet, or in the East without preparing to meet competition. Compared with other industries it is a grown man though by no means a giant. In tonnage it is almost as large as the salt production, 2,962,715 tons, and well over double the newspaper production, 1,175,554 tons. Compared with other products known as chemicals it stands second to the greatest, fertilizers.

	Production.*	1916.	Value.*	1916.
Fertilizers	5,240,164 tons		$92,369,000	
Sulphuric acid	2,748,527 "	6,085,444 tons	16,779,000	$73,514,126
Sodas †	947,576 "		18,305,000	
Muriatic acid	122,360 "		2,120,000	
Nitric acid	68,717 "		6,820,000	
Acetic acid	29,000 "		1,390,000	
Phosphoric acid	25,145 "		973,000	
Hydrofluoric acid	4,014 "		346,000	
Boric acid	2,778 "		296,000	

* United States, 1909.
† Soda ash, sal soda, bicarbonate of soda and caustic soda.

Uses of Sulphuric Acid. The uses of sulphuric acid are as follows in about the relative proportion given:

	Per Cent.
Fertilizer manufacture	51.9
Petroleum purification	11.7
Pickling iron and steel	8.1
Alum manufacture	4.6
Mixed acid manufacture (greatly increased by war)	4.1
Muriatic manufacture	3.2
Textile industry	3.1
Nitric manufacture (greatly increased by war)	3.1
All other uses	10.2
	100.0

For fertilizers, acid of 50° to 60° Bé. is used both in the manufacture of phosphate fertilizers and in the manufacture of ammonium sulphate. Likewise for the pickling or cleaning from oxide scale, 60° acid is generally purchased, although of late years the higher purity, together with the lower freight and cheapening of high strength acid, has led to the purchase of considerable contact acid for this purpose.[1] For dyeing and electroplating, as well as for the manufacture of many chemicals, the weaker acid may also be used. Acid of 66° Bé. is most largely consumed in the purification of petroleum, recovery of rubber, manufacture

[1] Also the use of contact acid in making nitric has led to the production of As free niter cake, now largely used in hot solution for pickling steel, for which purpose it has advantages over acid.

of explosives and in making mixed acid to be used for this purpose. For the making of mixed acid, however, the 98 per cent or oleum is being more largely used, since it permits the use of a weaker nitric and greatly decreases the cost of nitric acid manufacture without materially increasing the cost of the sulphuric. Spent acid (or mixed acid which has been used in nitration) is sometimes repurchased by the nitric acid manufacturer. It can, to a considerable extent, be used (with stronger sulphuric) for the manufacture of nitric. Ninety-eight per cent (as well as 66°) is also used in purifying certain fats and greases, and fortifying weaker acid and weak nitrating mixtures in the manufacture of pyroxylin products. Oleum, or acid stronger than 100 per cent, is used most largely in making mixed acid for the manufacture of explosives, and using the entire output of the nitric plant, in making organic sulphonates and organic dyes, the manufacture of other chemicals, and in fortifying or strengthening acid weakened by reduction, so that the acid may be used again.

Cost of Manufacture. It is wise also to keep always in mind the intrinsic commercial values of materials. No mistake of the young engineer is more fatal to his success than the loss of the practical man's confidence incident upon a proposal to "kill flies with an 18-inch gun," as one of them expressed it.

The manufacturing cost (including interest on plant, amortization, repairs, raw materials, labor, miscellaneous and "overhead charges") varies in this country from about $5.50 per ton of tower acid (about 60°) to $9 for 98 per cent when made from waste smelter gases. As made from purchased ore for the chemical trade, costs vary from about $6.50 per ton of tower acid to between $9 and $12 per ton of H_2SO_4 in the form of 66° acid or 98 per cent. At present (1918) about 20 per cent higher.

Sales prices vary from $7.50 to $10 per ton of tower acid and from $12 to $20 per ton H_2SO_4 for high strengths according to quality, kind of package, size of shipment or contract, freight allowance, etc., "what the traffic will bear." These prices are generally quoted per 100 lbs., 1/20 of a ton, so quotations on "66 o.v.," for instance, will be upward of 60 cents. In 1915 and 1917 prices twice to three times as high.

Properties. The strong acid is a heavy, oily liquid, practically colorless, odorless when pure, but generally smelling strongly of SO_2 generally present in excess when the acid is formed. Its density approaches 1.9 times that of water at 15° C., the weak acid boils with evolution of water and the concentrated acid finally boils at a temperature of about 290° C. with decomposition into water, SO_2, SO_3 and oxygen. The strong acid has a heat capacity about one-third that of water and freezes in the neighborhood of 10° C. Strong acid and oleum have a powerful dehydrating action, breaking down the skin and many organic materials by robbing them of water, and in some cases carbonizing and blackening them. Severe burns produced by sulphuric are best treated by the instant application of large quantities of water. Unless large

quantities are available the acid should first be wiped away with something dry before washing, as the heat of dilution with small quantities of water or with alkali accentuates the burn. Quick removal of the acid, washing with water and after treatment with an emulsion of sterilized sweet oil and lime water or ammonium carbonate makes a satisfactory treatment. For the eyes bicarbonate of soda should be used instead of the stronger alkali.

Corrosive Properties. Sulphuric acid with commercial impurities attacks practically all metals including platinum. The attack on platinum, however, is ordinarily very slow. On iron it is slow for acid exceeding 65 per cent, on lead for acid less than 65 per cent. Heat increases the rate of corrosion in all cases unless the boiling point of concentrated acid is exceeded. Gaseous acid, water, SO_2, and small quantities of SO_3 do not strongly affect either lead or iron, but condensation must be avoided or the strength of the condensate, if any, carefully considered. Liquid or dissolved SO_3, however, has a peculiar action on cast iron, appearing to enter the pores and disrupt the casting, sometimes with a violence approaching explosion. Steel, semi-steel and to some extent malleable iron castings may be used as substitutes in this case. Corrosion by the liquid acid of wrought iron pipe is much less than that of steel, but it is to be remembered that nearly all pipe sold as wrought iron is really steel pipe. The great hygroscopic action of sulphuric is an important factor in corrosion of vessels and pipes. If air be allowed free access to the pipes the acid rapidly dilutes itself by absorption of moisture from the air and corrosion proceeds quickly. Where iron and steel are concerned, therefore, the air should either be dry, or as far as possible excluded.

One fact should always be remembered: corrosion of metal goes on to some extent under nearly all conditions; more or less hydrogen is produced and it is extremely dangerous to use an exposed flame or a worn electric wire near such vessels without insuring the absence of "knallgas." Washing out with water should be avoided as much as possible and done only after previous emptying and cleaning from mud. Then an excess of commercial hydrated lime, powdered quicklime or even air-slacked lime or soda ash may be used, but certainly a powerful stream of water should be intermittently supplied and the vessel allowed to empty itself completely at frequent intervals until the water is neutral. In sending workmen into such vessels the possibility of asphyxiation should always be guarded against.

Sources of Raw Material. Three principal sources of sulphuric acid are, native sulphur, sulphide ores and those gases which were formerly wasted in technical work, from smelters, etc.

Sulphur. Crude sulphur for making sulphuric acid comes from two principal sources: volcanic deposits of Sicily and underground beds in Louisiana and Texas. So great has been the development of these that imports have ceased. It occurs chiefly mixed with limestone, supposed to have

been produced with the sulphur by the reducing action of carbonaceous matter and heat on calcium sulphate. There are numerous scarcely developed deposits of this nature in the United States.

In Sicily sulphur is mined on the south from Cataisia to Girgeute. It is separated from the gangue by fusion and distillation,[1] and came into the American market as dirty yellow lumps of irregular shape and size. The Louisiana deposits are attacked in a peculiar and ingenious way by (Frasch [2]) boring and piping the hole, forcing down high-pressure steam to melt the sulphur deposit around the end of the pipe and then supplying air to raise the mixed column of water, air and sulphur to the surface.[3] The sulphur thus obtained is of a better quality than much of the imported article. Texas properties are mostly similar.

A fair idea of the purity of crude sulphur may be given by the following analysis of a product worth about $18 to $20 per ton. S = 95.4, Ca, Sr. Mg. all figured (as Ca) 1.5, $SiO_2 = 1.3$. The Louisiana sulphur is 99.6 per cent pure and sells for about $22.

Pyrites. Pyrites, FeS_2, carrying often more or less CuS is, at present, by far the largest source of sulphur for acid making. Its use began about 1830.[4] Considerable quantities are imported, chiefly from Spain,[5] Portugal and Newfoundland. Prices (1918) 16–17 cents per unit L.T.

Deposits in the United States have been developed in New York, New Jersey and several of the southern Appalachian and far Western States. Most of them are not as high grade as the imported ore, but some are of the finest character.[6] Copper, zinc, calcium, magnesium and sometimes lead are objectionable from the point of view of the acid maker, as they retain sulphur that oxidizes to sulphate and is not available

[1] See "Mineral Industry," Vol. VIII, p. 592.

[2] U. S. Patents 461,429, 461,430 and 461,431 of 1891.

[3] See *Eng. and Mng. Jour.*, Dec. 14, '07. Day Allen Willey, p. 1107.

[4] Lunge, " Sulphuric Acid and Alkali," third edition, Vol. I, p. 36.

[5] Analysis of some Spanish ores with cost at works 100 to 300 miles from seaboard are given for comparison per 100 lbs. of sulphur contained in the ore.

	S.	As.	Cu.	Fe.	Pb.	Zn.	Gangue.	Price
Rio Tinto lump	49.69	.72	3.12	44.01	.86	.38	.....	.82
Rio Tinto lump	47.95	....	....	....	....	....	.....	.55
San Tolmo	49.9	.11	1.7	43.8	....	....	6.2	.59
Zalamea	49.4	.39	.46	46.21	.47	.12	.....	....
Peruna	45.	....	....	....	....	....	.....	.81

Prices are generally made "per unit," which means per ton per per cent of sulphur. Peruna, therefore, at 81 cents per 100 lbs. of sulphur would be $16.20 per short ton of sulphur. This means $7.29 per ton of ore. If $1 freight had been paid, this makes the selling price $6.29 per short ton of ore which would be quoted at $6.29 ÷ 45 = 13.9 cents per unit (short ton.)

[6] Numerous analyses of United States ores are given in Lunge, "Sulphuric Acid and Alkali," third edition, pp. 57 et seq. Prices (1918), 17–22 cents per unit L.T.

for burning. The lead and zinc otherwise interfere, by volatilizing. For roasting to produce SO_2 the per cent Cu×.505+per cent Ca×.799+ per cent Mg.×1.31+0.6 (const.) may safely be deducted from the analytical per cent of sulphur in the ore to ascertain the probable actual sulphur value. But this is by no means all, as it is not proper to value ore directly in proportion to the amount of sulphur available. Allowances must be made for the increased cost of handling the gangue both as ore and as cinder, and for the larger installation and repairs required where low grade material is used. Also the losses in cinder are absolutely larger with low grade ores, but even the same loss (say 2 per cent) is equal to 4 per cent of the total sulphur in a 50 per cent ore, 5 per cent of the total sulphur in a 40 per cent ore.

Waste Gases. The third source of sulphur is waste gases, particularly the "fumes" from sulphide smelters. In smelting zinc and copper ores a quantity of SO_2 is produced which is also turned into acid. These gases are otherwise at present worthless and are in many places a source of great expense to the producers, owing to damage suits by those whose crops or trees are injured thereby. This damage is denied, but the fact remains that the vicinity of a sulphide smelter is desolated. This source of sulphur for acid production promises to exceed all others.[1]

Sulphur Burning. In burning sulphur three points chiefly have to be considered: i.e., freedom of the gases from volatilized sulphur which has not been oxidized, sufficient richness of the gases for profitable operation of the sulphuric-acid making portions of the plant, and as complete removal as possible of sulphur from the slight residue of mineral matter. It is a familiar fact in domestic economy that sulphur used for sterilizing does not burn up completely. Provision must be made for maintaining a sufficiently high temperature of the surrounding walls and of the

[1] Careful study of the question for years leads me to believe that (in practically all cases) it is feasible to recover such fumes, that marketable products can be profitably produced in any locality where large smelters now operate, that the value thus produced will in many instances exceed that of the metal produced, and that no other phase of the sulphuric acid industry is so important. A single company at two plants is at present wasting enough sulphur to nearly equal the sulphuric production of the United States, and defends damage suits and injunctions in preference to developing the probable outlets for chemicals it might produce. Zinc smelters located in the Eastern and Central States have already profited largely by the use of this former waste. Two copper companies in the South have done something in the same direction, producing 450 to 500 tons a day where they will ultimately produce several times this amount; but when there is no ready sale for acid as such, "policy"(?) prevents the development of methods for utilizing these sources of sulphur. The smelter gases vary considerably in strength of SO_2, contain much dust and metallic oxides, sometimes precious metals, as well as considerable quantities of carbon dioxide and some carbon monoxide.

(1917) This source promises some day to be the largest. It is already about one-fourth of the total. Recent work on treatment of soils with sulphuric acid will create a hitherto undreamed-of outlet for "smelter acid." Sulphur can also be recovered from these gases by the Thiogen process at an estimated cost of about $12 per ton. (Bureau of Mines Bulletin 133 of 1917).

material on which the sulphur is supported. For the latter purpose an iron plate is generally used—cast iron preferred and it should be heavy enough and hot enough to insure active combustion of the sulphur at all points, even where the collected mineral residue is practically all that is left and only a small percentage of sulphur is being burned out of it. For this purpose special ovens are constructed. Provision is generally made for the preliminary heating of the iron pans, and when once lighted the burners should either be operated in battery or fed continuously, so that the variations of operation of the single burner shall not directly affect the strength of the gases to any material extent. The necessity for accurate draft regulation is apparent. Too much draft is better than too little if ample provision has been made for the complete interaction of the gases before they are allowed to cool. In some types of burners, in which the gases are drawn away too quickly from the burning pan, an excessive supply of air serves to chill the vapors and promote the deposition of sulphur in the flues. The indication of such action may be found in cloudiness of the Glover acid or filming with sublimed sulphur in the chambers. A modern type of furnace to be recommended consists essentially of a steel shell on rollers driven by motor (or shaft) provided at one end with mechanism for feeding the sulphur and regulating the draft and on the other with a combustion finishing chamber and means for admitting additional air. The sulphur fed in solid form melts with the heat of combustion in the cylinder and burns in a thin layer all over the inside surface of the walls kept wet with molten sulphur by the steady rotation of the cylinder. Fig. 74 illustrates another modern type of sulphur burner, which operates more like the Herreshoff or Wedge burners for fine pyrites discussed later.

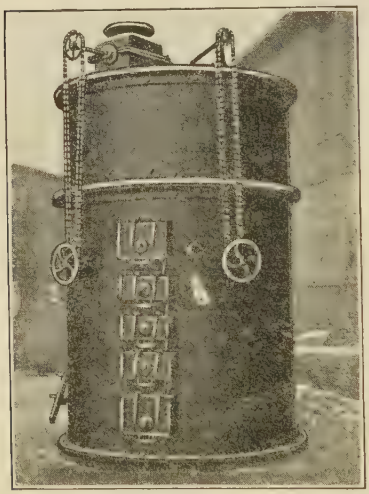


Fig. 74.

Burning of Pyrites.[1] Like coal, pyrites ore was not recognized as a combustible until early in the last century, various claims dating from 1793 to 1820. Probably the necessity of desulphurizing cuprous pyrites in the works of Perret et Fils and the exhaustive work done by them is

[1] One curious effect of the war conditions in 1918 is the fact that sulphur has temporarily superseded pyrites in many plants and may supersede it permanently if the sulphur producers are alive to their opportunity. To-day it is being used more fully even in fertilizer plants than for many years, i.e., about 20 per cent of the present enormous production of acid is already being made from brimstone.

mainly responsible for its success. The heat of combustion must be conserved, and therefore considerable masses are required to maintain the fire. As with coal, a certain weight (two to three pounds) can be burned per square foot of grate per hour, the depth of fuel bed (on top of cinder) generally varying from 10 to 30 ins. Excessive charges lead to loss of sulphur in the cinder, excessive depth of fuel to improper composition of gases and scarring or fluxing, which corresponds to the formation of clinker in an ordinary coal fire.

The first step in the burning of pyrites is to properly adapt the size of the ore to the character of burner being used. Although ore may be purchased on contract relatively free of fines or small ore, it is generally desirable to render the plant as independent as possible of market conditions. Added crushing machinery for reducing all ores to fines and burning it all in this condition, may even be preferred. The cost of crushing and grinding in a well-designed plant is small, the labor of crushing is less than the increased labor of operating lump burners, and furthermore the cinder from fines ore is always better burned, and the waste of sulphur in this way is always smaller with the same composition of ore. Properly operated they are without question more economical, but they present certain drawbacks which should be recognized.

First, the greater amount of dust produced and in consequence thereof the greater volume of the dust chambers.

Second, the greater cost of repairs for most types of the burners themselves, as they require more or less frequent renewal of rakes or rabble blades, and at long intervals some of them require a complete renewal of all arches. The crushing machinery also requires continued repairs, and many manufacturers prefer not to thus involve themselves. It is, however, generally possible to obtain a sufficient quantity of fines for regular delivery at attractive prices.

Crushing Ore. If run of mine ore is purchased, lumps may exceed 12 or 14 in. diameter and a heavy breaker of the general Blake pattern, illustrated[1] in Fig. 2, should be provided and located preferably below the ground level. Feeding should be done from an iron sheathed plank or cement floor. If lump ore is to be burned the product of the breaker should be elevated to a rotary screen of punched metal plates of $\frac{1}{4}$ to $\frac{3}{8}$ in. in thickness the holes in which being $\frac{5}{8}$ in. in diameter. The amount of fines made will be dependent upon the diameter of these holes, the character of the ore and the speed of the crusher. Five-eighths inch holes with a crusher running approximately 100 R.P.M. will produce from 12 to 30 per cent of fines. From the rotary screen, or riddle, the fines should be allowed to fall into a small hopper, and the lumps into a larger one. If all ore is to be burned as fines there should be placed, preferably below the breaker, one or better two sets of rolls illustrated[1] in Fig. 4, and the breaker should be set somewhat closer. The breaker

[1] Made by G. V. Cresson Co., Philadelphia, Pa.

may then be expected to reduce the ore to about $1\frac{1}{2}$ to 2 in., the first rolls to 1 in. and the second rolls from 1 to $\frac{3}{8}$ in. or less. For the delivery of fines ore to fines burners a belt conveyor is well adapted, and link-belt carrier conveyor with tripper has been used.

Weighing the Charge. For lump burners the charges are required to be weighed with moderate accuracy; this is best done by drawing directly from the hopper into the small industrial car standing upon scales specially introduced into the track for that purpose. The charge for each burner is thus separately weighed and dumped before the burner.

Lump Burners. The lump burner is nothing more than the simplest pattern of deep-bed coal fireplace. As, however, the value of its work is dependent on the production of a rich and reliable gas, too much care cannot be given to its exterior tightness, the ability to regulate drafts accurately, and to shake out the cinder evenly. Also, as it is designed to produce hot gases for concentrating acid, the loss by radiation from both burners and flues should be as small as possible. In the long run constructive economy at this point is apt to be false economy. The money spent in thoroughly encasing the burners and properly insulating them will pay large interest.

Fig. 75 shows a good type of burner, in which the common flue is provided with a double arch top. All doors are either hinged or their faces inclined, carefully planed, and therefore swing by gravity or latch against the planed edges of the door jam, allowing little leakage. The ash pit door *D* is perforated with 7 or more 1-in. holes, which can be plugged to regulate the admission of air below the grates. This arrangement is found more satisfactory than a wheel or slide damper because the adjustment is less likely to be displaced by accident. The doors *E* admit the shaker to the grate bars and also permit, to some extent, barring near the grate level. The doors *C* are likewise provided for the latter purpose, raising large scars to the surface of the bed, but are ordinarily not often required and may be made of the slide pattern and puttied tight if desired. Through the door *B* the charges are introduced, and distributed as quickly as possible over surface of the fire bed. The upper doors *F*, also slide doors, are not open except for occasionally cleaning the upper flue and may therefore be puttied up between times. The cross-section of the upper flue should be carefully figured to avoid rapid currents of gas that would interfere with the exit of gases from the individual burner. These burners are generally built from 4 to $5\frac{1}{2}$ ft. wide and 4 to 6 ft. from front to back.

Niter Potting. Fig. 75 also shows one method of potting niter (for supplying the nitric oxides to the chambers). The nitrate of soda and sulphuric acid are charged through a tightly covered hopper *K*, into the cast iron vessel *H*, which is supported on a plate in an enlargement of the common flue. Being thus subjected to heat from the burner, the nitric acid is distilled out. The door *J* is provided for removing the

entire vessel. The vessel may also be provided with a spout and a greater excess of sulphuric acid used, so that the mixture remains fluid while hot.

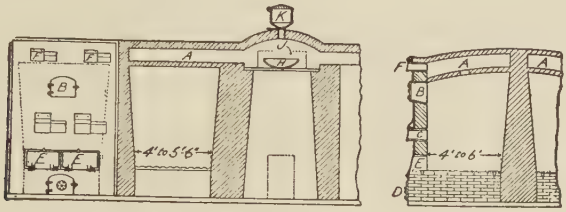


Fig. 75.

and can thus be run out when a temporary clay plug is removed. If niter is to be potted in this manner it is best to provide a number of pots operated in rotation and at short intervals; but the most satisfactory way of supplying niter to the chambers is generally in the form of weak nitric acid. The manufacturer of sulphuric acid located where no nitric acid is made, cannot generally buy at satisfactory prices or afford to pay the freight on it for this purpose, and is therefore reduced to the potting of niter.

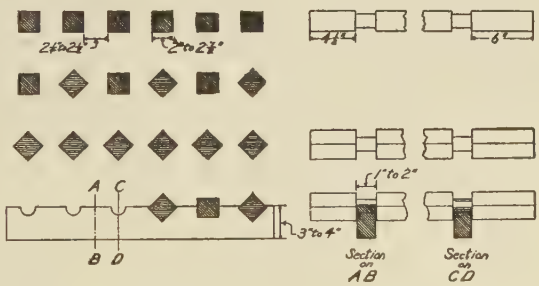


Fig. 76.

Grate Bars. Grate bars, detailed in Fig. 76, may be made of either cast or wrought iron, the latter being more expensive, but in many instances more satisfactory.

Shaking. Shaking is done by a crank handle shaker, which is sometimes provided with two handles equidistant on opposite sides of the center rod, so that both hands may be used or two men may operate the shaker. Alternate bars across the burner are generally shaken and the intermediate bars at the next period with such additional treatment as is required to evenly bring down the cinder. This cinder is generally allowed to accumulate in the ash pit, and is removed once in twenty-four hours with a view to reducing the amount of air allowed to leak into the burners. From 500 to 900 pounds can be handled in each burner in twenty-four hours, dependent on the quality and richness of the ore. Both for economy of construction and saving of heat, burners are generally built in double lines back to back; it is surprising what a difference in operating two or more such double lines can be noted between the operation of those burners which face one another and the burners on the outside facing

the walls of the building. Good insulating burner walls are important—second only to stability of construction.

Operation of Lump Burners. The burning of pyrites

$$2FeS+5\tfrac{1}{2}O_2=Fe_2O_3+2SO_2+2O_2{}^{1}$$

well illustrates a type of combustion which is extremely easy when draft is properly regulated and sufficient mass of the material is involved, but which was for many years regarded as impractical because the exact conditions required were misunderstood. Unlike coal, practically all pyrite is fusible. Too active a combustion, i.e., too free a supply of air in a large fuel bed produces too high a temperature (about 900°), causing the pyrites to melt and "scar" or clinker, cementing the unburned lumps together, sometimes enclosing them entirely, thus rendering it practically impossible to burn them until broken up, and impossible to pass them through the grates. A precisely similar result attends insufficient draft in certain localities of the burner, particularly in burners of large size. In this case the high temperature results not from too rapid combustion but from too small an excess of air to carry away the products of combustion as well as the excess of heat at surrounding points. The temperature theoretically obtainable by combustion of pyrites exceeds 1000° C., which is considerably in excess of that required to flux any of the usual grades of pyrites. The entire secret of success in pyrites burning, lies in proper regulation of charge and draft to suit the other fixed conditions of design of burner and character of ore supplied. Fortunately one excellent guide is always available, the analysis of the gases produced by the burners. This analysis should, when everything is running properly, be made at least twice a day while, if difficulties are being incurred with the burners, it is well to make such analyses hourly. With so many variable factors to consider it will perhaps simplify matters (after making the setting tight) to fix the draft at such a point that the analysis of the gases shall lie between 5 and 8 per cent SO_2, and should the burners then be too hot, carry a shallow bed of fuel. This is secured when already operating by omitting or greatly reducing a few charges without proportionately decreasing the amount of cinder shaken down, until hot cinder appears, after which the amount of cinder shaken can be reduced to equality with the smaller charge. Both draft and charge should then be increased gradually until the capacity of the burner is obtained. Herein lies the value of being able to determine what percentage of sulphur may reasonably be expected as inevitable in the cinder from a

[1] Numerous secondary reactions occur, such as direct oxidation of FeS, CuS, ZnS, etc., to sulphates, followed in the case of iron by decomposition into FeO and $2SO_3$, when the temperature reaches approximately 550° C. Similar reactions occur with copper, but at a higher temperature. With zinc it is necessary to raise the temperature to a bright white heat. Hence the sulphates once formed in the burners cannot be decomposed without danger of melting the pyrites.

given ore, and the necessity of daily or at least semi-weekly determination of sulphur in the cinder.

All work that it is necessary to do with the burners should be done as rapidly as possible, so that doors may be open the minimum time. The successive rotation of the burners should be as regular as clock work. If the number of burners in a set (frequency of charging) is such that two burners are to be charged at once they should always be as nearly as possible diagonally opposed to each other on opposite sides of the set, and the rotation should be so arranged that the period of greatest heat occurs in burners half the length of the burner set from each other. No red-hot ore should ever come through the grate bars; in fact, working with any usual depth of fuel bed, the ore when shaken down should be fairly cool. Proper burning of the cinder is superficially indicated by lightness, porosity of surface and a clear red, brown, or black shade (according to the character of ore) with little evidence of mottling, streaking or apparent hard spots. When broken the ore should show no kernel, or hard center but should have substantially the same texture throughout, except right at the surface it is likely to be more porous and frequently is checked by numerous cracks.

Fines Burners. The early designs of narrow staggered shelf burners, and broad shelf burners rabbled by hand, need hardly claim our attention to-day in view of the extent to which the mechanical furnace has been developed. McDougall Bros. started the development of the circular or rotary fines burner in the seventies in England at about the same time as Perret in France. Modifications were made and patented from time to time by these inventors, by Mackenzie, Frasch, Herreshoff and others. The two latest and most perfect rotary patterns are the air-cooled O'Brien and the water-cooled Wedge burners. Even though the former is almost a toy compared with the latter it fills its place in smaller works, burning 5 to 15 tons a day. The best running capacity of the O'Brien on high grade ore smaller than $\frac{1}{2}$ in. is about 6000 to 7000 lbs. per day. The same furnace can properly burn 9000 or even 10,000 lbs., but repairs become excessive. Wedge furnaces range from 12 to 32 ft. in diameter, with 5 to 7 hearths. The $21\frac{1}{2}$ ft. furnace has a capacity of 28,000 to 48,000 lbs., and weighs about 304 tons.

The O'Brien Burner. Fig. 77 shows the O'Brien burner, the mechanical features of which need little explanation. The central shaft A is cooled by the vertical current of air passing up through it. The arms B are likewise hollow and subdivided lengthwise nearly to the outer end in such a manner that a portion of the current of air is drawn out sidewise through one side and back again to the hub by the draft of the central shaft acting as a stack. The arms are secured by hubs C tightly fitting into the central shaft. The inner end of the arm tapers, is inserted with the blades D turned sidewise and locks with a quarter turn on its own axis in the direction which the drag of the ore on the blades along its bottom

tends to continue. Thus the action of rotation around the central shaft tends to lock the arms more firmly into the hubs, at the same time they can be turned up in the opposite direction by a special tool, removed and replaced in a few minutes. The rabble blades are cast as part of the arm, and given an angular position. They are carried around the central shaft, slowly moving the ore outward or inward on the alternate shelves. The shelves raked inward have an opening *E* around the central shaft through which the gas passes up and the ore falls down. The alternate shelves have openings *F* at the periphery for the same purpose. A screw feed from the hopper *G* gives an excellently regulated supply of ore and the cinder passes out through the bottom chutes *H* that supply a portion of the air for burning. Two doors *I* are provided to each shelf for removal of arms and have wheeled draft openings *J* that serve also as peep-holes for observing temperatures. Access to these peep-holes and to the top of the burner is provided by iron-side ladders, and a movable working platform of wood serves when removing the rake arms. The hot air from the burner shell and the central shaft are profitably used in thoroughly drying the ore. Rotation is imparted to the shaft *A* by a very cheap and simple gear which is nearly the whole diameter of the burner and is made by bolting segmental sheets *L* of $\frac{3}{16}$ in. steel to a flange *M* on the lower end of the shaft, uniting the periphery of the circular plate thus formed with cheap cast-iron sections of curved racks *N* which in turn rest upon small pinions *O*. If anything catches inside the burner the weight of the rack becomes insufficient to keep the gears meshed and the racks jump without breaking or injury, only making enough noise to call attention quickly to the trouble. A vertical chain drive *P* actuates the large sprocket on the screw shaft *Q* from the main pinion shaft below.

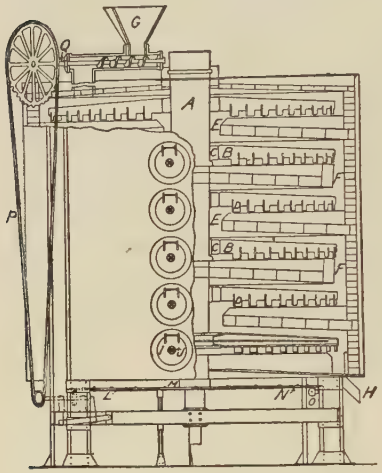


FIG. 77.

The Wedge Burner. The Wedge burner, Fig. 78, is naturally more substantial in every respect, as required by its heavier duty. The central shaft *A* is large enough to admit a workman, its temperature being at all times low enough to permit his making any repairs that may be necessary. Each arm *B* is separately water-cooled and strongly secured to the shaft by a heavy breech block *C*, also water-cooled, while the rabble blades are individually removable and replaceable with practically no interruption of the furnace. The hearths are level and have openings *E* near the shaft and *F* at the outer edge for dropping ore and permitting the rise of

gases. The entire top of the burner G serves as a combined feed hopper and feed table, being provided with its own special arms and tripper rakes that swing back under the excessive load of deep piled ore, thus regulating the feed at the center even if the ore is piled high at the sides, at the same time gradually distributing such a pile evenly. The supply of ore entering around the shaft through a sand-lute continually renews the lute and further regulates the feed, cinder being discharged through the chute H. Repair doors I, poke and peep-holes J are likewise provided. The central shaft, all arms and moving parts are supported on the gear M, by means of the four roller bearings N, traveling on the smooth outer face of the gear, the hole being merely centered by the bottom pin P giving a rigid central shaft with no "steppe" or base block, practically without wear, friction being almost wholly rolling. Obviously the feed is here strictly dependent on the operation of the rake arms and over feeding or clogging is almost impossible, as is also the failure of the water-cooled arms. Nevertheless the driving pinion O is actuated by a shear pin in the hub of this pinion that cuts off if any serious obstruction takes place in the furnace.

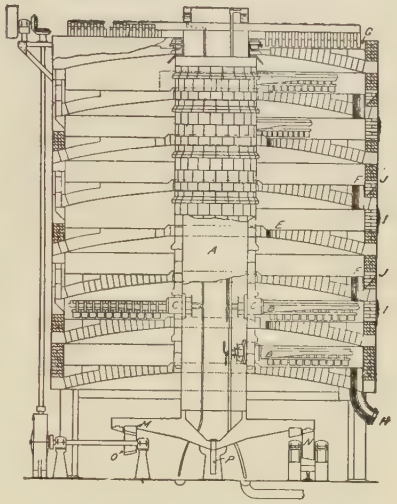


FIG. 78.

For the burning of special ore, zinc blend, etc., particular types of furnaces have been devised, but it is not within the province or space allotted for this work to consider them in detail.[1] Other types of fines burners are built on the drag conveyor principle or reciprocating rake principle, but are less used than the rotary furnace and less practical for most purposes.

Operation of Fines Burners. Mechanically the operation is extremely simple, consisting of feeding substantially equal quantities of ore in equal periods of time by means of a ram, screw, rake, or similar device. The regularity of the feed is of great importance so that conditions effecting it, i.e., speed of shafting, etc., should be properly controlled. Nearly all types of burners make the feeding device subsidiary to the rotating mechanism, stopping the feed in case for any reason the rotation ceases. This is most perfectly done in the Wedge furnace. The skipping of the O'Brien only calls attention to the trouble. While it is obviously necessary to prevent the clogging up of the burner, it is not by any means the only requirement. A 10 per cent variation in the speed of shafting

[1] A number of devices for this purpose are indicated in Lunge's "Sulphuric Acid and Alkali," and in the special books on metallurgy.

either reduces the capacity of the burners or results in unconsumed sulphur. For most acid making purposes the air enters cold partly through adjustable openings in the doors and partly through draft openings in the bottom, gases increase both in richness and temperature in passing up through the burners, taking a long alternating course from the center to the periphery and back again for each pair of shelves. The rotating mechanism carries the stirrers, scrapers, shoes, ploughs or rakes, as they are variously called, set at an angle alternately pointing inward and outward, so that while the general movement of the ore is circular on each shelf, it is also spiral toward or away from the center. Also it is turned or rolled upon itself in such a manner as to expose all portions of the ore, and being finely divided the best possible access of oxygen to the unconsumed sulphur is permitted.

Starting the Furnace. Starting of the furnaces is carried out in much the same way with lump or fines burners. When new they should be dried out slowly with small wood fires and a good supply of air, but with no violent draft. This requires from two to four weeks. The fires are then rebuilt on a cinder bed and forced steadily until the burner becomes red hot. The burner is then quickly cleared of large pieces of wood and the supply of ore started. Suspension of operation or hold-overs cannot be much prolonged with the smaller burners unless special precaution has been taken to jacket them against heat losses and provide most carefully against the leakage through doors. If this is done the fines burners hold over quite satisfactorily from two to five days according to size; lump burners hold over longer. Minor repairs to the burners require no hold-over, but should repairs to an arch be necessary, it is apt to necessitate a complete shut-down and overhauling of the burner for which no period of hold-over would suffice and for which any considerable heat in the burner would make working impossible. The special tools furnished each type of burner require no particular description as their uses will be specific to the type of burner and almost obvious from their mechanical construction.

Regulation of Furnaces. Certain general instructions may be given for regulation of fines burners. The distribution of temperatures from shelf to shelf is regulated by increasing the draft to raise the heat zone or by decreasing the charge when the lower shelf becomes too hot with the central hot zone too low. Sulphiding of rabble blades indicates too little draft or too rapid charging. The O'Brien burners are apt to show slightly decreased capacity in hot (summer) weather, less noticeable in the larger burners. Wedge burners can be operated on pretty wet (almost sloppy) ore, but the O'Brien burners do not give their capacity unless ore is fairly dry—the drier the better. Very wet ore affects the Wedge capacity somewhat, but very much less because of the large hopper area of the top and the drying action that takes place there. One great advantage presented by the large burners with their enormously long

travel of ore is the conversion of SO_2 to SO_3 by the partly burned ore itself. As much as 10 to 15 per cent of the SO_2 may be so converted with a consequent increase of chamber capacity and greatly improved action of the Glover tower. Great care should be taken not to overload.

Dust Prevention and Collection. As has been stated, the use of fines burners is advantageous in most respects. Proper design and selection can overcome all serious objection to repairs. But the quantities of dust usually carried over into the Glover are objectionable. Little attention has hitherto been given to its prevention, but much to its collection. Without considerable expense for operating fans, *complete* purification of hot burner gases from dust may as yet be regarded as practically impossible.

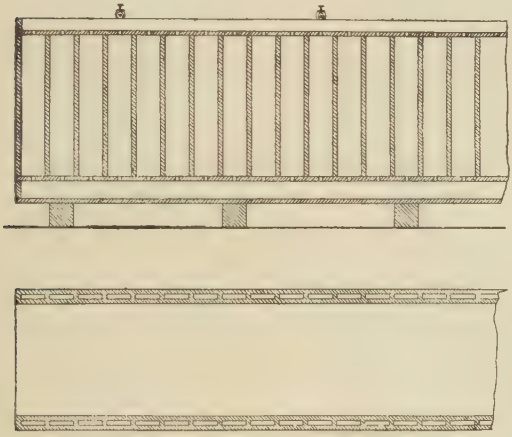


FIG. 79.

Water-cooled Flues. Of the older styles of dust separators Fig. 79 shows a water-cooled flue, in which the velocity and temperature of the gases were reduced, thus depositing the dust. In these enlargements the gases were supposed to come nearly to rest and lose the velocity which enabled them to carry the particles of dust along. They were found to be only moderately successful.

Baffle Plate Separators. Baffle walls or plates were then introduced, Fig. 80, and found to give much better results on very fine dust. Unfortunately their introduction subdivided the settling space and increased the velocity of the gas currents again. Numerous vertical partitions or curtains parallel to the direction of the gases, Fig. 81, with dampers for alternately shutting off one side while cleaning, also gave good results, but were by no means satisfactory. The material had to settle too far and vertical currents circulated within the divisions, owing to differences of temperature of the sides or top and the bottom.

Centrifugal Separators. A. P. O'Brien ("Mineral Industry," Vol. 9, p. 632) introduced a centrifugal dust separator, Fig. 82, entirely feasible wherever a fan is used and giving excellent results for all larger sized dust. He adapted it to serve also as a niter oven, by introducing through the conical body *A* cast-iron pots *B* that were hardly calculated, however, to improve the centrifugal action. The pots can be conveniently charged from the top and emptied from the bottom. Dust is discharged from the apex of the conical bottom without interrupting the operation.

Only about 75 per cent of the dust from fines burners was recovered.

Modern Separators. Early in the efforts to purify gases for the contact system it was observed by workers here and in Europe that burner gas drawn through a 1-in. pipe into the laboratory showed practically no contamination of the contact mass. As will be seen later, this means a degree of purity which is almost absolute freedom from suspended matter. This peculiar method of purifying gases by slow flow through pipes of small diameter was pointed out by Knietsch in 1900 in his account of the preliminary work of the Badische Analin und Soda Fabrik. Seeking, however, to avoid the multiplicity of small pipes that would be required by this method, Henry Howard, U. S. Patents Nos. 970,053 and 896,111 provides what has proven to be one of the best dust collectors yet devised. It consists of a series of horizontal parallel shelves an inch or so apart, across which the gases pass in a slow stream, from a general inlet chamber to a general outlet chamber. The results obtained are truly astonishing, even dust ordinarily regarded as impalpable being largely retained. No attempt has been made in the patent to cover the process of purification by passage through small tubes, and it is doubtful if this process would be patentable in view of the publication of Knietsch's results ten years ago. Some results obtained on a small scale indicate that the tubular form is an even more efficient purifier than the shelf, although of course the space occupied in the plant is not so efficiently used. Nevertheless it is apparent that a highly efficient dust collector could be so constructed.

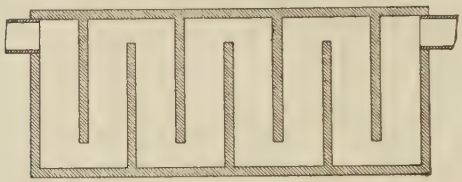


FIG. 80.

FIG. 81.

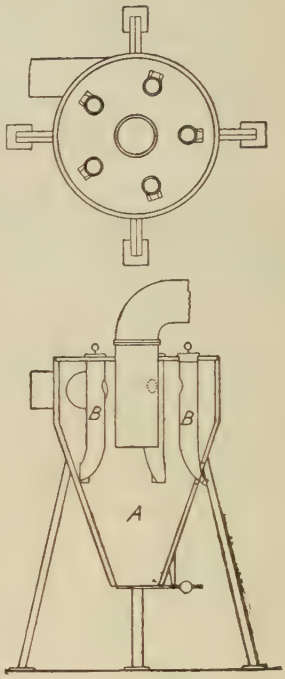


FIG. 82.

Likewise in contact process work it was observed that gases could be purified to a surprising degree by " filtration " through layers of small coke lumps, cinder from the burners, etc. Dust catchers which consisted in filtering the gases through cinder were at first quite unsatisfactory, because the cinder used was itself a great source of dust and no provision was made for interrupting or alternating the gas currents while shaking out the lower layers that became clogged with dust. The inventor of the Wedge burner has, however, met these objections and given us a dust collector free from these criticisms. On inclined grates are supported sets of filters consisting of beds of marbles $\frac{1}{2}$ in. in diameter and from 2 to 4 ft. deep. These make an extremely complete dust separation, much more so than irregularly shaped lumps and carry the collected material down with them.

Chamber Plant. The clearest understanding of the chamber plant will be obtained by first describing the general method of carrying out the process and then indicating modifications at one point or another with the changes in form of apparatus involved.

The sulphur gases obtained are constituted as follows:[1]

	SO_2	O_2	N_2	CO_2
Sulphur burners	11.0–6%	10.0–15%	79%	.....
Pyrites burners	8.5–5%	10.5–14%	82%	.....
Metallurgical gases	8.0–2%	10.0– 6%	.....	0–8%

The dust having been separated the hot gases enter at the bottom of the Glover tower (3), Fig. 83, and pass upward through packing or filling occupying the interior of this tower. Here they meet a down-flowing stream of aqueous sulphuric acid, evaporate the water from this aqueous acid and give up part of their heat in the process, at the same time supplying a portion of the steam required for the first stages of the reaction in the chamber proper. Higher up in the Glover tower this moisture and heat perform a further function in that they help to drive out the lower oxides of nitrogen from the " nitrous vitriol " fed into the top of the Glover tower along with the aqueous acid.

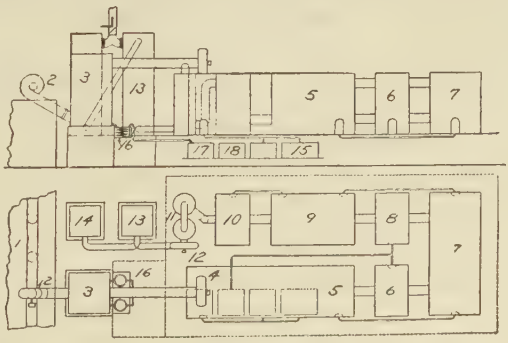


FIG. 83.

Near the top of the Glover is a favorite place for locating a fan (4)

[1] SO_3 varying from .2 to 2% is here included as SO_2 and O_2.

if none has preceded the Glover tower. At (4) the fan may blow horizontally, or vertically downward into the chambers.

It is customary to make the first chamber (5) fairly large, as the gases are at first converted rapidly. Removal of the end products by cooling and thorough mixing to facilitate further conversion becomes necessary. The addition of water in some form to take part in this further conversion does not arise until equilibrium is approached and the conversion begins to slow down. At this earlier stage in the process the corrosive action of the gases is greatest and it is not desirable to expose too great a surface to deterioration. The gases are generally, therefore, introduced into the large chamber (5) wherein approximately one third of the conversion is expected to take place. Some heat is removed by conduction and radiation from the walls and ceiling, condensation occurs on both these surfaces and to some extent incipient condensation in the mass of the gas, owing to the formation of acid of a strength which is not volatile, which therefore tends to precipitate in mist or rain, so that in the later part of their passage through a large first chamber the gases require more moisture either as steam or spray. Personally the writer doubts the relative value of very large first chambers.[1] From the first chamber, in which approximately one-third of the acid is usually produced, the gases pass to other chambers (7) and (9) and towers (6), (8), (10) which may be empty or may be provided with suitable packing or with perforated plates designed to promote the mixture of gases and moisten them by supplying acid or water at the top of the tower. The use of cold liquid sprayed into chambers or fed to intermediate towers (6), (8), (10) greatly increases the ability to remove heat from the gases and makes up for the absence of conducting and radiating surfaces lacking in the larger sized chambers, or shut off by acid-proof lining of the towers. Large empty

[1] Ten years ago Lunge prophesied that towers would largely, if not wholly, replace chambers, and in the last three years the first "chamber" systems without chambers have been successfully operated. The Opl system, originally introduced at Hruschau, Austria, showed that a lower cost of installation ($\frac{2}{3}$) or a larger capacity ($\frac{1}{3}$) were to be obtained, that much less ground space was required and all acid produced as 60° Bé., in addition to which it appears as though the tower plant would be easier to supervise.

The typical plant to make about 20 tons 60° per day would consist of six (possibly eight) towers, 10 feet square and 40 feet high, connected in series top to bottom and each provided with distributors, all filled with packing, and finally of a fan and filter-box. The first three towers operate like Glovers, the last half more like Gay-Lussacs, e.g., acid rich in nitrous vitriol from the last (No. 6) is run down the first tower, that from No. 5 down No. 2, and that from No. 4 down No. 3. Nitric acid is added on No. 2 and water on Nos. 2, 3 and 4. About 4 k.w. are required for the fan, the consufmpton of niter is given as 352 pounds 36° or 0.46 per cent, that of air as 140,000 cubic feet of 60 pound air, and of cooling water 7000 cubic feet of cooling water. (1918) No great progress.

Another satisfactory plant seems to have been operating in England for more than a year, but what results can be secured in various strange hands, and how the repair costs will be affected by the strenuous tower conditions, remain to be seen.

[2] Where one tower alone is used it is generally filled with coke, specially made acid-proof stoneware shapes, or pumice stone.

chambers are more commonly used, or large chambers without packing, but alternated with high narrow chambers packed either with the Lunge-Rohrmann plates, or with some arrangement of bricks or tiles found to be cheaper. The purpose of any special arrangement is:

1. To promote the mixture of the gases.
2. To expose the largest possible surface of liquid to the gases.
3. To vary the temperature of the liquid surfaces as frequently and widely as possible.
4. To provide sufficient space (time) for practically completing the conversion of the SO_2 to H_2SO_4, under the conditions to which the particular design subjects it.

These chambers are followed by a cooling device consisting of either unpacked towers (11) or of a long flue connecting the chief reaction space with the apparatus for recovering the lower oxides of nitrogen after they have performed their function in uniting the SO_2, O, and H_2O to form H_2SO_4. Between the last chamber and the final (Gay-Lussac) towers is another preferred location for a fan (12) when used to furnish draft for the system. This absorbing apparatus (Gay-Lussac tower) (13) is frequently duplicated by a second Gay-Lussac (14) to insure complete recovery of the lower oxides.

From the Gay-Lussac the gases now almost completely purified from both SO_2 and oxides of nitrogen are finally discarded through the stack. A fan is sometimes used here. If mechanical draft (a fan) has not been introduced somewhere along the line it is customary to introduce either a steam jet or a damper in the stack for regulation of draft. It is always best to provide both.

Having followed the passage of the gas, the equally important movement of the liquids should be considered. Sulphuric acid is formed in the last chamber by the bringing together of SO_2, O and H_2O by means of the oxides of nitrogen. It is precipitated upon the walls and collects on the floor of the chamber, being the weakest (48° to 50°) and purest acid made in the system. From here it is sometimes taken directly for separate concentration when a purer acid than ordinary chamber acid is required. Generally it flows forward into the next chamber where it is slightly strengthened by the stronger acid made in the warmer chamber, but it is also slightly contaminated by the greater quantity of dust settling there, the greater action on the lead walls and the greater amount of As_2O_3, etc., in the gas. And so on down the series of chambers until it reaches 52–54°. Thence it may be partly withdrawn for use and sale or for separate concentration, or taken to the storage tank (15). Most, if not all, of this acid may be elevated from the tank to the top of the Glover tower (3) and mixed with "nitrous vitriol" or run in through the sealed openings to mix with "nitrous vitriol" in the upper zone of the tower. At first it is concentrated by mixing with the nitrous vitriol and then diluted from the steam condensed by the two cold acids. It also loses by

conversion any excess of oxides of nitrogen or SO_2 it contained, and helps to liberate the lower oxides from their solution in the 60° "nitrous vitriol." Meeting the SO_2 of the burner gases the nitric and nitrosyl sulphuric are decomposed and the resulting oxides of nitrogen carried along by the burner gases. As it trickles down the acid is further heated by the hot gases and soon begins to lose water rapidly and becomes concentrated, flowing from the bottom of the tower into coolers (16) with strength of between 59 and 61° Bé. This is the "Glover tower acid" containing most of the arsenic and dust from the ore that is not held back by the dust catching devices (1). It generally contains a little SO_2 and is nearly free from oxides of nitrogen though quite capable of dissolving them readily when cold. A portion of this strong acid is elevated to the top of the Gay-Lussac tower (14) where it trickles down against the outgoing gases, thus dissolving and recovering the final portions of the nitrous gases not absorbed in the preliminary Gay-Lussac (13). From the bottom of the Gay-Lussac tower the acid flows to a storage tank (18). The excess of this circulating acid formed by the continual addition of weaker nitrous vitriol from (14) is the strong nitrous vitriol that goes to the top of the Glover (3) and returns the recovered nitrous gases to the cycle of the process.

Reactions in the Glover Tower. The gases as they come from the burners usually contain from 6 to 8 per cent SO_2, 0.5 to 1.5 per cent SO_3, 8 to 12 per cent O_2, a little H_2O, some dust and nitrogen and are hot. With large dust chambers their temperature may be as low as 150 to 200° C. The hotter the better, however, for the work the Glover has to do. The reactions liberate much steam so that about half the moisture required for the chamber process is carried along with the lower oxides of nitrogen and SO_2 into the chamber. If the acid is diluted to about 58° Bé. (74.35 per cent) nearly all niter is liberated, at which SO_2 greatly assists in acting on the niter itself. It is customary, therefore, to feed the top of the Glover with cold 60° (77.67 per cent) acid used at the end of the process (Gay-Lussac tower) for recovering the lower oxides of nitrogen, and also with water or chamber acid, preferably the latter, because the mixture can be more readily made outside the Glover with less heating and without evolution of nitrous fumes and because the chamber acid is thereby concentrated in the Glover instead of so much useless water being introduced into the system where it is not needed. This strong "nitrous vitriol" and the weak acid are often separately fed into the top of the Glover tower (3) through properly trapped holes, but are often mixed outside or just as they flow in. The cold acid condenses and absorbs steam rising from the lower part of the Glover and the packing of the tower should be of a character to facilitate their mixture and the heating of the liquid, but not to facilitate it too soon. The liberation of these lower oxides in the Glover tower along with the moisture, gives us immediately the conditions requisite for the formation of sulphuric acid and,

in a well operated and designed tower, there is accomplished here nearly 20 per cent of the total formation of acid of the chamber plant. To secure this and at the same time to secure freedom of the acid at the bottom of the tower from the oxides of nitrogen, several conditions are requisite.

First, the mixture of strong and weak acid should be equal and thorough.

Second, this mixture should penetrate to some degree below the top of the tower before being subjected to too much heat.

Third, sufficient heat (120° F.) should then be applied to insure the rapid evolution of lower oxides of nitrogen in the presence of SO_2 and ample moisture before the liquid has penetrated too far down the tower. It is not rational, to use the same material for the entire filling of the Glover tower. Three distinct operations are to be carried out therein. At the top of the tower the nitrosyl sulphuric acid from the Gay-Lussac and weaker acid from the chambers is to be mixed together with any nitric acid that may be used for maintaining niter content of the system. Just below this mixing zone should occur the zone of heating and reaction, the reaction extending back up through the mixing zone and into the chambers. Next we have the zone of combined concentration and denitration in which the latter predominates. Up to a strength of approximately 59° Bé. sulphuric acid can be denitrated by hot sulphurous acid gas, but unless the acid is somewhat weaker, the reaction is not complete even in the presence of considerable water vapor from the concentration going on in the bottom of the tower. It is, therefore, desirable to have the acid reach the zone of final denitration not stronger than 58° Bé. The nitrogen compound most permanently resisting the separation from the sulphuric is the nitrosyl sulphuric acid. The dissolved gases are removed very much higher up. The reaction by which the last traces of nitrosyl sulphuric acid are removed is probably as follows:

$$2NO_2HOSO_2+SO_2+2H_2O=3H_2SO_4+2NO$$

This NO together with the remaining water from the concentration below proceeds on up the tower and is quite capable of reacting under the existing conditions for a further formation of the nitrosyl sulphuric acid, or of sulphuric acid direct. The oxidation of NO in the presence of sulphuric acid does not proceed to N_2O_4 or HNO_3. Probably the NO reacts with the sulphuric as follows: $2NO+2H_2SO_4+\frac{1}{2}O_2=2NO_2HOSO_2+H_2O$ though under the conditions at the lower portion of the zone this reaction would be slight. Likewise $2NO+2SO_2+H_2O+1\frac{1}{2}O_2=2NO_2HOSO_2$, a reaction more likely to occur at this point. Owing to the conditions of high temperature and ample humidity, however, neither reaction is likely to proceed at all near completion and much NO will pass up the tower along with the oxygen and be converted into N_2O_3 by simultaneous absorption in sulphuric and oxidation.

Probably the reaction

$$N_2O_3+2H_2SO_4=2NO_2HOSO_2+H_2O,$$

takes place in the lower portion of this zone, and the reaction

$$N_2O_3+2SO_2+H_2O+O_2=2NO_2HOSO_2,$$

somewhat higher up. The gases passing into the upper zone of the Glover tower carry an excess of moisture and are excellently equipped both by moisture and temperature to work the reversible reaction $N_2O_4+H_2SO_4=NO_2HOSO_2+HNO_3$. Here they likewise meet a liberal supply of nitrosyl sulphuric acid brought from the Gay-Lussac towers mixed with the weaker chamber acid, which enables this reaction to be more easily reversed. The N_2O_4 resulting therefrom is in excellent position, therefore, to act upon any product in the upper portion of the tower immediately upon its entrance. The nitric acid added for the maintenance of the niter content of the system may well be the subject of this reaction for $HNO_3+3H_2SO_4+N_2O_2=3NO_2HOSO_2+2H_2O$. From the upper zone of the Glover tower, therefore, the gases pass off into the chambers at a temperature of about 60° to 90° C., generally under normal conditions about 80° C. with about 15 per cent of their SO_2 converted, laden with moisture and also laden with lower oxides of nitrogen.[1]

Below the mixing reacting and denitrating zones of the tower, begins the upper portion of the concentration zone. Here the gases contain so much SO_2 and are sufficiently hot and saturated with steam to eject from the down-flowing liquid all traces of nitrogen compounds, before reconcentration has progressed too far (58-59° Bé.), which would cause the acid to retain oxides of nitrogen. Finally at the bottom of the tower there should be sufficient zone of high temperature left for the concentration of all the acid to 60° Bé., preferably a little higher. To accomplish this, it is desirable to have a form of packing which shall not permit too ready down-flow of the liquid, but shall retain it to some extent so as to delay its passage through the hot zone long enough to permit its ample heating and concentration, while at the same time exposing sufficient surface of liquid to the hot gases to assist in the concentrating action. Herein lies the reason for conserving the heat by proper burner walls. This packing, however, should be sufficiently open in its structure to

[1] In looking over the reactions which have occurred in the Glover tower it is not surprising that careful calculation indicates the oxides of nitrogen to have taken active part in one reaction or another approximately nine or ten times in a manner calculated to produce sulphuric acid. Therefore it is again not surprising that even in the relatively small space of the Glover tower, from 10 to 20 per cent of the total sulphuric acid "make" of the chambers is produced, an activity per cubic foot one hundred or two hundred times as great as in the chamber. Nor is it surprising that even distribution of the acid, both nitric and sulphuric, containing nitrous oxides must be maintained at the top of the Glover tower.

run no risk of becoming blocked up by the deposition of flue dust which has succeeded in passing the dust chambers. Ample dust recovery can be made by modern methods without reducing the gases below 400° C., since their usual temperature from lump burners ranges from 500° to 800° C. and from fines burners 450° to 600° C. It is generally safe to rely on gases being from 350° to 450° C. as they enter the Glover, and some sets, even mixed fines and lump burners, exceed this figure.

Construction of the Glover Tower. The tower (Fig. 84) must, therefore, be constructed to withstand the severest duty. The almost universal practice is to make it of lead with joints constructed, as are the joints of the chambers, etc., throughout the plant, by burning the lead together (autogenous soldering). For this purpose the lead (always first scraped clean where it is to be burned) is lapped, and a small oxy-hydrogen or oxygasolene flame directed simultaneously against the edge of the outside sheet and a "strip" or stick of lead held in the other hand. The lead of the Glover is protected inside with the utmost care both from heat and corrosion.[1]

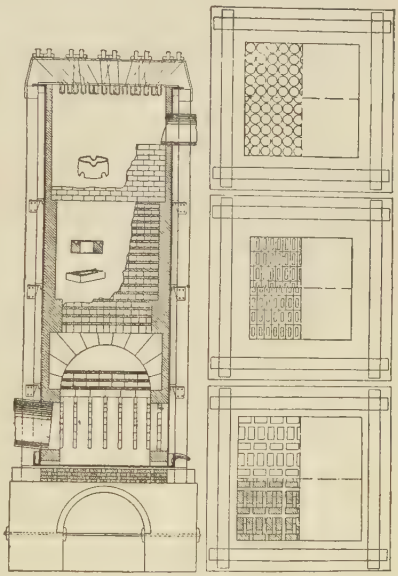


FIG. 84.

As the framework itself and the tower with its packing, top house and supply tanks at the top make a heavy load, a firm foundation of masonry becomes necessary. The foundation, or platform, should be well pitched, asphalted or preferably in the former case, covered with a thin layer of pitch and sulphur melted together. Then the whole top should be protected by the acid pan of 16 lb. lead. Wooden tower frames are very common and the sill may then serve as the edge against which the drip acid pan is turned up and over. Yellow pitch pine should be used and the sills and column feet may profitably be well pitched in setting, and dowel pinned.

There are two ways of joining the sheets for sides or curtains of a Glover tower, usually depending on whether the tower is square or circular. In the former case it is customary to suspend sheets from the top of the tower and make the joints vertical, avoiding the location of a joint close to a corner. In the latter case it is customary to

[1] Recently (1915–1917) many towers have been constructed entirely of close-laid brick, but some of these have given serious trouble. Undoubtedly this construction can be successfully used, but should be guaranteed and most carefully inspected.

make hoops or belts slightly smaller at the bottom and to lap each inside the one below. Square towers are sometimes made in this way. At the top of the tower the sides are bent over the strong frame which is intended ultimately to support the greater portion of the weight but the sides must also be secured to the diagonal bracing or horizontal cross pieces of the tower frame by frequent straps to prevent their being sucked in or pressed out as the draft may act upon them and also to take a portion of their weight from the top of the frame. As a rule the sides are allowed to hang within the upstand of the bottom dish and it is generally stated that this is necessary in order to allow for expansion and contraction. The fallacy of this is indicated by the fact that the sides are attached rigidly to the heavy inlet pipe for the gases at the bottom of the tower and that no provision is made for the rise and fall of this pipe.

The inlet pipe for the gases presents great difficulties because of its large diameter, the high temperature of the gases and because of the necessity of making the joint tight with the curtain instead of with the heavier and more rigid basin. The pipe conveying the gases from the burners is almost universally made of iron. It is preferably made about 12 to 18 ins. larger than the volume of gas requires and is then lined with brick. At some plants the connecting piece extending into the tower is made of volvic lava, shaped to fit the end of this iron pipe. The volvic lava pipe consists of an upper and lower piece and extends clear through the side of the Glover tower and its lining. A lead or iron pipe is sometimes used to cover the volvic lava and join with the iron pipe from the burner. At other plants a heavy piece of stoneware is used instead of the volvic lava and must be similarly encased. The easier way and one which has proven entirely satisfactory in many installations is that shown in Fig. 84. The heavy iron pipe which conveys the burner gases to the tower is often, and the writer believes should always be lined with brick, and this brick lining is carried straight through the lead connection to the tower, through the lining of the tower to the inner chamber, care being used to lap the brick joints of the lining as tightly and as far as possible. To support this lining during construction and afterwards to give rigidity to the connection with the tower an unflanged piece of iron pipe is inserted as shown and the flange of the burner pipe is rabbeted to receive it.

Tower Packing. Until recently the usual method of beginning the tower packing was to lay a single layer of brick over the entire floor of the tower directly on top of the basin. In harmony with modern steps for the further protection of this basin, the bottom of the tower is now more commonly covered with two or three layers, breaking joints, sometimes split brick being used for the lower layers. For even distribution of the gas within the tower a considerable chamber must be left at the bottom. For this purpose and to support the chief weight of the packing, a heavy lining wall is made up higher than the top of the inlet opening. In large

towers several piers, or perforated or arched walls are carried up to the same height, to serve as supports for the grid. It is customary to make this lining from 18 to 24 ins. thick. Above the top of the inlet opening it is then reduced in thickness, leaving a shelf 6 to 9 ins. around the inside of the tower level with the tops of the center piers or walls. In arranging these walls care must be taken to distribute the gases evenly over the entire bottom of the tower and not to obstruct their passage. Resting on these piers and ledges the grid is then laid in place. This grid may consist of deep narrow beams of volvic lava or of acid-proof stoneware. It is sometimes made of a series of narrow arches. The latter construction is in more common use abroad and the former is believed to be more prevalent in this country. A second grid is sometimes laid across the first to distribute the weight, or a second set of arches to facilitate cleaning out from below. The spaces between the ends of the grid beams should then be filled up with lining brick to prevent the grid pieces from falling over sidewise, likewise where the grids join on a pier or wall. The selection of the brick or tile is a matter of great importance as it is expensive to repack a tower. Selection should be based on actual experience with the material in a Glover tower, or recommendation by an expert. Upon this bridge begins the actual packing of the tower from the chemical or reaction point of view. The lining may consist of large lumps of quartz approximately 8 to 10 in. in diameter at first, and later of smaller sizes. Pumice stone or lava pieces shaped to the sides and filled with graded pieces have been used with great success, also acid-proof brick. Ridges of dust, however, are apt to form on the flat upper surfaces of the brick so that they should always be used on edge. In some cases the deposition of flue dust is very heavy indeed and necessitates the opening of the towers and the washing down with acid, cleaning out at intervals every one or two years. Properly constructed, however, there is no need whatever of such frequent cleaning. If, therefore, bricks set on edge are used for the lower portion of the packing for the first couple of feet they should be set apart as widely as possible, and it is best to begin the packing with specially large tiles. Where lumps of either lava or pumice are used, they should at first be of large size, 12–18 in., and should be carefully laid so as not to obstruct the gas passages and so that the sharper corners are upward to prevent the lodgment of dust. The packing material of Niedenfuhr-Lunge illustrated in Fig. 84 has all the advantages of the brick except economy. In fact, it is better in almost every respect than the brick filling but is probably too expensive for ordinary use. A diamond-shaped brick set on edge and with the edges notched out to rest down over the bricks below, has been very successfully used for this purpose in a number of plants. It leaves practically no surface on which dust can collect, as the surfaces have an inclination of about 60° to the horizontal. The inclined sides of this brick are slightly ribbed in order to produce resting places for the acid and ragged edges over which

the uprising currents can pass sharply, pushing out the liquid and exposing as much surface as possible. One criticism to be made of the diamond sectioned brick is that they do not retain sufficient quantities of acid (lack of great porosity) to permit of a gradual surface concentration and diffusion of the weaker acid and to delay the passage of the liquid down through this section of the tower by their absorptive or retaining qualities, In this respect pumice or lava would be more advantageous, but the surface exposed by the diamond-shaped brick is many times that which could be obtained by the ordinary rough shaping of lava blocks or lumps unless they were specially dressed to about the same shape and size as the rhomboidal brick. Like all special packings, however, these rhomboidal bricks are expensive, being approximately 11 cents each.

At the top of the tower the temperature has generally fallen to about 100° C., and it is no longer necessary to protect the lead so carefully from the action of the gases. Nevertheless it is as well to carry a portion of the thickness of the tower lining up practically to the top of the tower; $4\frac{1}{2}$ in. or even $9\frac{1}{2}$ in. is desirable, merely as a general protection for the lead and as a semiporous surface for interaction. The actual top plate or lute-plate of the tower is not so subject to heavy wear and tear because it is largely cooled by the incoming acids and being always located somewhat above the outlet from the tower, is at the top of a dead space.

The top plate of the tower is shown in Fig. 84, in which are small depressions or cups located all over the top, arranged so as to occupy little room in order to secure as many such sources of supply as possible with the limited area of the tower top. Each of these cups is, as a rule, oval and provided with a division wall separating the oval into two equal acid-receiving cups. At the bottom of each of these half cups is a small pipe extending down into the tower for a few inches and extending up into the half cup for from 2 to 5 ins. according to the taste of the designer. Lead thimbles or short pipes with one closed end and serrated open edges are inverted over these up-standing pipes and complete the liquid lutes. When acid is run into the depression it must fill up for a height of 3 or 4 ins. before acid can flow into the tower at all, and the pipe through which it flows is of such a diameter that it flows down around the edge in a thin stream rather than sucking in with a rush. Any method which will supply all of these half cups, one side with a small regular stream of nitrous vitriol and the other with a small stream of chamber acid, will give us a good distributing system. Ordinary cocks on the pipes to regulate each stream are out of the question, as they plug up and it is practically impossible to regulate the size of the stream accurately. The usual system of making the subdivision is that indicated in Fig. 84, where a series of lips are dressed over on one or both sides of a straight or circular trough and each of these lips is permitted to slightly overflow, the size of the stream being easily regulated with a very great minuteness by a slight tap or blow above or below on the crest of the lip. Each of these little

streams has a pipe to convey it to the proper point at the top of the tower.

On the floor above the head of the tower (in order to secure the head for a constant and steady flow to the towers) is located the tank and generally also the level apparatus. It is customary to make the top and sides of the tower very much lighter lead than the bottom. About 16 lb. lead is generally deemed heavy enough. It is false economy to so reduce the thickness of lead that a renewal of any portion of the tower will be necessary. Good policy demands that the tower be so built, like the "wonderful one horse chaise," that when one piece requires repairing, the whole thing may as well be taken down.

The Capacity of Glover Tower. It is found desirable to maintain, at least approximately, a certain fixed relation between the size or capacity of the Glover tower and the size or cubical capacity of the chamber installation. Opinions as to this relation vary somewhat and should in any case always be expressed in terms of actual working volume of the Glover tower and not of the total space within the lead. Experience has indicated that if the tower is properly packed there is no gain obtained by extending the net height of actual packing, more than about 20 ft. Consequently the size will be a matter of variation in cross-section rather than in height. This cross-section has in some cases been as great as 25 or 30 ft. in diameter without detriment to the action of the tower. About 300 or 350 cubic feet of actual Glover tower packing space is allowed per ton of sulphur burned per day.

Acid Coolers. The acid running away from the bottom of the tower and coming from recent contact with the hot gases will, as a rule, be very hot (about 130° C.). Even when the burner gases are cool it is about 100° C. It may be higher, but as 60° acid begins to boil, at about 180° C., a much higher temperature than 150° cannot reasonably be expected. Nor is it desirable, because under most conditions all of this acid must be cooled either before storage or before its return to the Gay-Lussac tower for absorption of nitrous-vitriol. For this purpose there are generally located just below the bottom of the towers cooling worms or tanks. Sometimes air coolers are used. As far as possible the hot acid should be kept out of contact with the lead until the latter is cooled on the other side by moderately cold water, otherwise the wear and tear on the lead coolers will be heavy as was explained in describing the corrosive properties of acid, Fig. 85 illustrates one of the most convenient devices for cooling of Glover tower acid (where water is moderately scarce). A wooden tank is built cross-divided into a number of compartments, tightened up with bolts and lined with 6 lb. lead. Along one side of it is a lipped trough of stoneware sections backed with asbestos millboard and beaten into an 18 lb. lead trough covered with wood. In each of the compartments is placed a nested coil of 1 in. AA lead pipe provided at the inlet end with a Buchner

or silica funnel extending down into the end of the coil below the top surface of the water. The bottom end of the coil is brought up over the edge of the tank so that the coil always stands full of acid and the various turns of the coil are separated by flat irons suitably bolted together in order to make the coil a rigid unit. Each compartment is provided

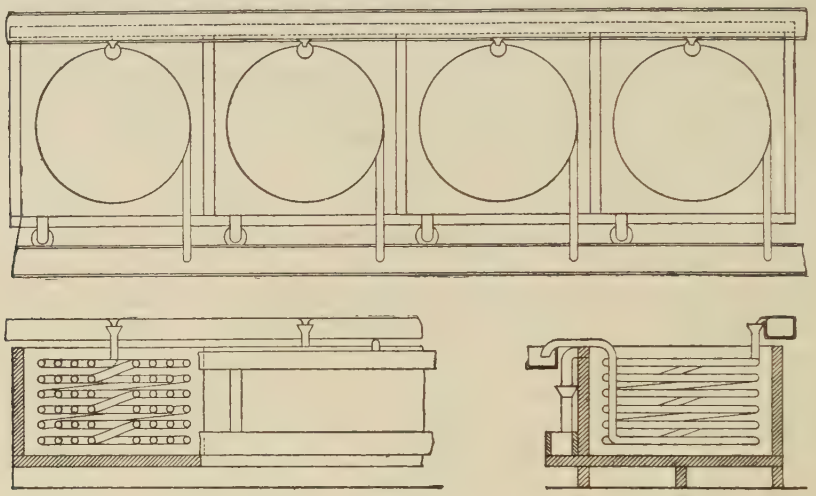


Fig. 85.

with a separate plug in the bottom and a trough underneath by which it may be entirely emptied of mud or water in order to wash it out or permit the examination of the coil to establish its tightness. Each coil is separately fed by a short syphon lying in the lip from the hot acid gutter at the back and each discharges separately into a cold acid trough at the front (or back) of the system. Beneath this cold acid trough is located the wider water overflow trough the top of which is tightly covered to prevent steaming. A daily litmus test of the overflow of each tank reasonably insures the absence of serious leak in any one of the coils. If a leak is suspected the corresponding syphon may be lifted without seriously upsetting the action of the several other coils and the coil in question can be lifted out by a chain-fall, removed entirely from its box, and a reserve coil placed with very little delay. If the leak is certain it is not even necessary to remove the water from the box.

In another type of cooler (suitable for ample water supply) the action of the extremely hot acid upon the lead pipe is almost wholly avoided by having in the tank sufficient volume of cooled acid to mix immediately with the hot acid flowing in before it comes in contact with the cooling pipes. In this manner much longer life is secured for the cooling pipes. The flow from the Glover is divided into only two streams (two being necessary in order to permit repairs to be made to one of the devices). Two large tanks are located below (and sometimes within the

Glover foundation) and are lined with 16 lb. lead. Inside of this lining and supported on lead-covered iron frames are large flat coils of 1″ AA lead pipe, which are independently supplied with cold water and planned to maintain a layer of cooler acid at the top into which the hot acid flows. Below this level the acid is slowly and steadily settling downward to the bottom of the tank cooled everywhere by the lower portions of the various coils, and as the water is fed to all coils at the bottom this portion of the acid obtains the prolonged benefit of the coldest water available in the system. This finally cooled acid from the bottom of the tank is drawn over by a syphon to the Glover acid storage tanks. In order to prevent the acid from being too much heated by the surrounding liquid, the syphon-pipe is itself surrounded by sewer-tile or other stoneware pipe, sometimes two layers being used and the space between the pipe and the tile packed with asbestos fiber. Similarly the pipes carrying the cold water down to the bottom of the coils may be covered with insulating pipes if this is necessary, but generally no such precaution need be taken. Unless the Glover tower is set very high (so that the space available under it is great) it is preferred not to locate the tank under the Glover because it must be made too shallow for the most efficient working, or the storage tanks beneath the chambers become too low. It is better to allow space (either beside the Glover or between the Glover and the first chamber) on a separate platform about 6 feet below the level of the Glover tower for devices of this character. This brings them nearly on the level of the chamber floor, not more than 2 or 3 feet below it at most, permits the flow of the acid from the cooling devices by gravity to the storage tanks and still permits the elevation of these storage tanks above the ground high enough to locate all acid eggs below them without much excavation.

Storage Tanks. Tanks for the handling of acid are generally made of timber lined with 6 or 8 lb. lead. It is desirable to have in each tank at the head of the tower several hours' supply of acid for the tower in question. The tanks at the bottom of the towers both for Gay-Lussac and Glover acid should have at least a day's capacity and the tanks for chamber acid may have any desired capacity according to the method in which the acid is to be used. These tanks may all be satisfactorily located under the chambers and should be covered or provided with a sub-roof under the chamber floor and located if possible far enough from that floor to allow of access to the floor for examination when necessary. Cooling of the acid is generally required for the Glover tower acid only. In some plants it is thought desirable to cool the Gay-Lussac acid, but usually this is unnecessary, unless the Gay-Lussac acid is to be recirculated or a portion of it used in intermediate towers.

Chamber Reactions. Turning now to the chambers, it is well to consider briefly the general types of reactions which are expected to be performed therein. Several theories of the operation have been sug-

gested and it will be interesting to present these and consider them briefly.

Davy, observing the presence of NO_2HOSO_2 crystals and the necessity of water for the reaction, proposed the explanation that $2SO_2+3NO_2+H_2O=2NO_2HOSO_2+NO$ forming droplets in the chamber atmosphere which sink into the acid at the bottom and are diluted thereby, water being condensed on the side curtains in larger proportion and diluting this bottom acid. On dilution

$$2NO_2HOSO_2+H_2O=2H_2SO_4+NO+NO_2$$

which partly oxidizes $2NO+O_2=2NO_2$ again to unite with more SO_2. The objections to this are that so much more water condensation is not observed on the curtains and instead of there being much more NO and NO_2 near the bottom they seem to be evenly distributed through the gases.

Berzelius and others, including Peligot, Weber, and Raschig, regarded the formation of nitrosyl sulphuric as wholly accidental or abnormal.

Lunge, Hurter and Sorel substantially agree that

$$N_2O_3+2H_2SO_4\rightleftarrows 2NO_2HOSO_2+H_2O,$$

calculated the theoretical rate of formation in close agreement with fact, and suggested circulation of drops through varying conditions of temperature and practically constant H_2O and N_2O_3 vapor tension. $H_2SO_4.2H_2O$ passes to the central hot zone, is concentrated, takes up N_2O_3 to form nitrosyl, passes to cooler sides, absorbs water decomposing nitrosyl and forming sulphuric 67 per cent near walls at $75°=27$ mm. At center 90°, 27 mm.$=73$ per cent. Observations confirm these facts.

The particle of aqueous H_2SO_4 floats about in the chamber gases, being carried up in the middle and down at the sides; on the one hand, owing to the heat of the reaction and, on the other hand, owing to the cooling action of the chamber sides. These particles of acid are alternately subjected to higher and lower temperatures. When the temperature is raised concentration increases by evaporation and the acid is able to absorb or retain greater quantities of N_2O_3. This N_2O_3 when absorbed from the surrounding medium may carry SO_2 in along with it together with water or other constituents necessary to make sulphuric acid. Then on passing over and down along the chamber sides the particles are subjected to a more saturated atmosphere and to a cooling action which tends to condense moisture upon their surface. The moisture may have traveled side by side with the particles for many feet, but not have encountered conditions favorable to condensation. As soon as the moisture is condensed on the particles, thereby diluting them, the nitrosyl-sulphuric acid is decomposed, liberating the N_2O_3 and forming sulphuric acid which is added to the mass of the particles. Whether this N_2O_3 on its way out from the surface of the particles forms additional sulphuric

acid in any manner is not essential, but probably it does not. When liberated, this N_2O_3 travels side by side with the particles, the surrounding SO_2 and the moisture envelope, until the temperature is again raised in the middle zone, when more moisture is liberated from the particles and N_2O_3 is again taken up.

This is at least a clear view of what may go on during the greater portion of the chamber operation. Unquestionably during the early portion of the action at the entrance of the first chamber (when extremely rapid formation of sulphuric acid occurs) Glover tower reactions also occur.

Surface Contact. The importance of surface contact and impingement of gases cannot be denied or overlooked. In 1884 McTear (J.S.C.I., '84, 228) carried out an interesting series of experiments by placing a tray 12×12 ins. in the chamber and noting the amount of sulphuric acid collected on the upper surfaces of the tray and of glass plates supported over it. Taking the deposition of acid on the upper surface of the tray alone (700 grams per day) as unity, this deposition was increased 2.3 times by supporting in a vertical position above the tray 12 pieces of glass, 12×6 ins. wide, having a total surface approximately 12 times as great as the surface of the tray. When placed horizontally, 12 ins. wide and arranged as before, the deposition of acid was 4.5 times as great as that of the tray. It was found that a single vertical surface exposed to impingement of the gas condensed about 30 per cent more acid than the other surface and that a horizontal plate collected on both upper and lower surfaces very nearly as much as when placed vertical. This is a purely surface action. As early as 1861 it was suggested to make vitriol in a long channel filled with horizontally supported glass plates, but such an installation would have had too little permanence. Partitions of brickwork, of suspended glass plate and even chambers filled with coke have been tried. Steam aspirators, and even fans, have been used to circulate the gases about in the chambers. But to date the most successful method of mixing and cooling the gases and fixing the suspended liquid is the use of towers between the chambers. These towers may be supplied with a downflow of acid or other cooling means. Thyss and Sorel both attempted to use such towers (in the former case made of lead and in the second case filled with some sort of packing) before Lunge suggested plate towers. What is probably the best developed plate system is that of George Lunge and Ludwig Rohrmann, patented in 1886, 1887, 1889, the plates being placed so that holes do not register and the drops from the edge of one hole strike upon the plate below. Gilchrist has filled the tower with a number of horizontal cooling pipes of triangular section and allowed air to circulate through these pipes. The system has found great favor in many American plants. The smaller sizes of diamond-shaped bricks (rhomboidal packing) offer great advantages of surface and stability. The writer's experience with simpler and less

expensive packings, however, has been entirely satisfactory. The tower may be sprayed with ordinary chamber acid, unless the intensive system of operation is to be applied when nitrous vitriol can be profitably used therewith, but too great concentration should be avoided since we have here neither the high temperature nor the rich sulphurous gases to denitrate the strong nitrous vitriol. Re-circulation of these towers with a strength about the same as made in adjoining chambers is recommended.

Cooling also is certainly essential, as the formation of liquid cannot continue without heat dissipation. Cooling is so important that in England a nearly fixed relation between cooling surface (0.2 sq.ft. per cu.ft.) and chamber capacity is recognized.

As the reaction in the chamber progresses to completion, however, we may confidently predict from the general law of the mass action (common sense) that it will become slower. At the latter end SO_2 (and oxygen) becomes somewhat exhausted, the more exhausted or rare the SO_2 becomes the more infrequent will be the contact of SO_2 molecules with those of nitrosyl sulphuric acid or nitrogen oxide capable of making it. Thus in spite of any mixing or cooling or other action to which we may submit the gases we can be sure that reactions will be very slow at the end. About 30 per cent of the total weight of acid is made in the first chamber where a number of chambers (4 to 6) are used. Where only three chambers are used this is more likely to be from 30 per cent to 40 per cent and, with only two chambers, may be 60 per cent or even 80 per cent. With the larger number of chambers the last (No. 6) makes only 1 to 3 per cent of the total acid. With three chambers from 9 to 20 per cent of the total acid, and with only two chambers from 20 to 35 per cent or 40 per cent may be expected (these figures are all exclusive of the acid made in Glover and Gay-Lussac towers, the former averaging from 10 to 18 per cent and the latter in the well-operated chambers below 5 per cent).

Sight holes are used for observing the color of the gases for presence of moisture and niter. As the reaction progresses heat is necessarily liberated, becomes sensible as temperature, is partly dissipated by the walls, and gives an excellent indication of the operation. Thermometers are, therefore, very generally used.

Niter Control. As might be expected, niter is the important variable. A temporary cessation of niter supply will cause a rapid fall of temperature in the first chamber, as much as twenty degrees in a few hours, simultaneously affecting the strength of acid produced. The percentage of niter in the gases has the greatest influence on temperature, because within wide limits it controls the rate of production of sulphuric without necessarily at all affecting the yield of acid or the consumption of niter. The simplest indication of niter conditions is the color of the gases. In the first half of the travel (cubical space) white sulphuric mist and reduction by SO_2 to colorless NO prevent any color being observed. About the middle, however, a faint tint (yellowish N_2O_3), and before

passing to the Gay-Lussac, in fact, in the middle of the last chamber, a distinct red (N_2O_4) appears (not a clear red, which means dry gases, but a misty red).

The quantity of niter lost varies much with skill of operating and adequateness of recovery plant to the intensity of working. There is always some loss; never below 1.5 parts per 100 of sulphur burned = 0.5 per cent of the actual H_2SO_4 produced. This figure generally ranges from .75 to 1.25 however. With ordinary single Gay-Lussac and Glover 1.0 per cent is good working and 0.8 per cent is excellent. As the cost of niter is from 10 to 20 per cent of the total manufacturing cost of the acid, careful economy of niter is essential.

One of the first steps in "doctoring" a chamber is to make sure of ample niter supply. Deficiency is more objectionable than excess and is indicated by paleness of end chamber, decreasing nitrous strength of Gay-Lussac acid, absence of ferrous sulphate test first in middle or end bottoms, possibly by red fumes at exit (SO_2 to Gay-Lussac), decrease in quantity or strength of drips, presence of N_2O in exit gases, etc. The serious consequences are decrease of production, SO_2 escaping to the last chamber in too great quantity with moisture preventing proper formation of NO_2HOSO_2; formation of nitric and further removal of niter from the system, possibly complete reduction to N_2O not recoverable; passage of niter as NO with SO_2 to Gay-Lussac; absence of absorption added to decomposition of nitrous vitriol by SO_2 leading to loss of niter both in bottoms and at exit *because too little* niter is present.

Drips. "Drips" is a name given sample acid collected by troughs from the inner surfaces of side curtains or by trays clear inside the chambers and piped to the outside for testing. It slowly "drips" from these pipes. Weakness[1] of the drip means either too much water (when quantity will be full or excessive) or too little formation of acid (causing lower temperatures and also smaller quantity). Other things being right, the strength of drip serves as a guide to the admission of steam or spray. When the drip becomes too weak the steam supply should be sharply reduced for a time and then resumed. Too much water in presence of excess of oxygen reacts with the lower oxides to form HNO_3, the condensation of which on the chamber side is apt to be injurious. The glass sight-jars, or windows, should not be dripping wet, merely beaded over. Continued excessive supply of steam and consequent formation of nitric acid leads to too much nitric in the suspended acid which is carried down to the bottom acid, weakening the strength of the same and increasing its content of niter by the nitric brought down. This action is cumulative,

[1] The strength depends largely on the point of collection, 4 to 6° Bé., weaker near the surface of the chamber (owing to the cooling and condensation near the curtain) and stronger from the interior, unless very strong chamber acid is being made, when this difference will be less. It is almost obvious that the absolute strength of the drip is not so important as how the strength varies from day to day and from first chamber to last.

since the weaker acid on the bottom itself tends to hold more nitric. The yield falls off and consumption of niter increases. Action on the lead does permanent damage; white drips result. Also the chamber becomes pale. When the drip becomes too strong it may mean that the chamber is very rich in niter or that there is too little moisture. Another possible evidence of the absence of moisture is the presence of chamber crystals on the glass plates or lute covers. When the quantity of the drip decreases it is sure to indicate either an absence of acid manufacture or an absence of moisture. In the latter case the strength of the drip is apt to be high; in the former case the strength of the drip is low.

Draft. Draft should be primarily regulated according to analyses of gases at Glover entrance and at exit. Too much draft shows at burners by weak gas, while too little draft is indicated by the absence of O_2. Too much draft weakens the reaction and carries it back too far in the chambers, losing SO_2 and niter. Too little permits over-reduction and loss of niter, finally perhaps loss of SO_2, and certainly loss of profit on the investment. The passage of gas through the chambers as a whole, is observed with delicate pressure gages.

Chamber Construction. The following special principles underlie chamber construction and any chamber detail should be considered with each of them in mind.

1. Variations of pressure inside the chambers may amount to more than $\frac{1}{2}$ in. water column, or about 3 lbs. per square foot over the entire surface of the chamber so that precautions must be taken to prevent the side curtains from sucking in (or bulging) by frequent attachment of both the curtains and the top to a suitable framework.

2. Variations of temperature expand and contract the lead, so curved corners or movable attachments to the framework should be provided to permit movement without buckling or bending the sheets, particularly at joints.

3. The supporting and surrounding framework should be rigid. As the safe tensile strength of lead at 0° or 100° C. is only about 500 lbs. per square inch (a sheet being self-supporting for a height of about 90 ft.), shifting of the framework, failure of supports, or sticking of movable attachments produces destructive strains. In open-sided chambers, wind strains must also be provided against.

4. The corrosion going on continuously, though slowly, is augmented by higher temperature, excessive moisture in the gases, increased niter content, absence of SO_2, too rapid movement or impingement of the gases, or alternate action of liquid acid and gases. The points of most severe attack therefore are as follows: around the entrance to the first chamber, owing to the heat, richness and velocity of the whirl of gases circulating to join the incoming stream; the end opposite this entrance (if the first chamber is not very long) owing to richness and impingement of the entering stream; the whole of the first chamber because the temperature is

higher, the gases richer and reaction more active; any points where the sides are uncooled by the outside air, as points in contact with timber framework, the inner sheet of a lap joint, the bottom when it rests on the floor if it is not covered with mud or a layer of liquid, and side curtains where they descend inside the bottom pan; the last chamber where all SO_2 is pretty well exhausted, acid mist is much thinner and where in the absence of SO_2 the reaction $N_2O_4+H_2SO_4=NO_2HOSO_2+HNO_3$ takes place (or with excess moisture even the reaction $2NO_2H_2O+O_2=2HNO_3$).

Most of the chamber plants now in operation have wooden supporting framework of vertical studding crowned with a wall plate rounded on the upper inside edge and beveled away outward below the round. The lead side curtains bend out over the round, are nailed down to the plate and strapped to the studding. In this construction, seams are generally run vertically and either a large section or the whole side of the chamber, is burned lying upon the floor within the chamber frame and then hoisted into place, or burned at the top and let down after securing the edge to the plate. The side and end curtains being thus placed in position, a movable scaffold the width of the chamber is set up within the walls, the successive sheets of the ceiling are laid upon the scaffold, and the long joints burned three or four at a time. The ends of each sheet extending out over the side sheets where they turn over the plate are burned fast; straps are burned on the ceiling and attached to beams laid as the work progresses. The scaffold is moved along underneath leaving a finished ceiling. For convenience the scaffold is generally made to travel on wheels or rollers. Finally when the last sheets are placed the scaffold is dismembered into sections and removed between two of the side sheets which have been left unburned for a portion of their height. The floor is then well cleaned. The bottom sheets are laid clear across the chamber bottom turning up inside and over a rim of side boarding 18 to 20 ins. high in similar way on all sides, sheet after sheet being burned on as laid. The flues are generally left until the last and give entrance and exit holes for the workmen while engaged in laying the bottom, making the final clean-up before starting as well as testing the tightness of the work.

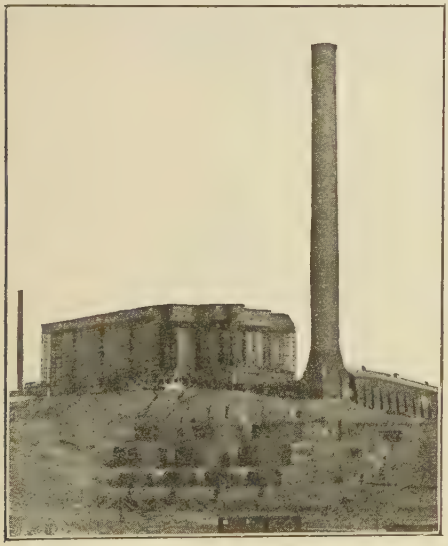


Fig. 86.

Figs. 86 and 88 show a more modern type of construction (although the wood is still much used) consisting of a steel framework. Chambers of this type are apt to be built of greater relative height and as seen, Fig. 88, a different system of attachment[1] to the framework is used. Incidentally it might be said that this attachment presents many advantages, since it can generally be located on the outer face of a joint and the point of attachment will therefore be better protected from corrosion within, by the lap. Laps are almost invariably burned on the outside edge so that the extra lead of the lap can serve to protect from corrosion the point at which the joint is made.

Connection of Chambers. In connecting the chambers one with another, circular or rectangular lead gas flues are used. It is generally preferable to make the flues circular because they can then be provided with longitudinal stays of wooden slats, easily enclosed and supported by iron rings. In some cases, however, square flues are much more desirable as a matter of convenience and engineering.

The connections between chambers have generally been taken from the lower portion of the end of one chamber to top of the preceding chamber. A great deal of experience, however, has indicated that it makes very little difference from what point the outlet, or to what point the inlet is taken. The natural circulation of the chambers is very quickly set up regardless of the height at which the gases may happen to be introduced. This is, of course, to a less extent the case when forced draft is used.

In making attachments for connections to the chambers and in making repairs, the curtains and the tops, as well as the connecting flues, may be freely cut into and changed. The greatest care, however, is used to avoid disturbing the bottom basin because of its very great importance in the storage of acid, and because of the extreme difficulty of repairing leaks in the bottom.

The various arrangements for observation, taking of drips, temperatures, level of acid within the chambers, etc., are as a rule scattered at different points throughout the chamber. There seems, however, to be no advantage in this wide distribution of points of observation and in some cases they have been concentrated together. For drawing off the acid from the bottom of any chamber a lead syphon is allowed to dip into the bottom pan where an alcove in the curtain allows sufficient space for it to stand. Acid is thus drawn from the chamber to a "boot" or pot set in the floor outside and made as high as the side boarding of the chamber bottom. Acid is drawn from each chamber to the chamber

[1] In the wooden frame it was noted that the plate is slightly overhung on the inside so that the lead should not touch the framework at any point. To prevent the sucking in by draft, or the pushing out, the entire curtain must be attached by lugs or straps to the framework. Such attachment unless slotted should not be made before the chambers are started up, because the elongation of the lead when heated will throw too much strain upon the straps.

preceding it, and a similar boot is almost invariably placed at both the outlet from the later chamber and inlet to the earlier chamber, the boots being connected by a pipe and each supplied with its own syphon. From the first chamber acid is drawn to the supply-tanks of the eggs or lifts to the Glover tower, and to the same or other supply tanks, possibly for use of the concentrating system where 66° acid is being made, though such acid is generally taken from later chambers because acid there is purer. Likewise alcoves are best made at the extreme ends of the chambers for drawing off. The writer prefers a single observation alcove with boot at each end of each chamber. The greatest care is generally observed to avoid making unnecessary holes in the bottom sheet of the chamber or doing anything to disturb the layer of mud over the chamber bottom and expose the lead to consequent corrosion. For this reason a sheet of glass or piece of thin tile is frequently placed under the bottom of the inner syphon-leg to prevent the flow from disturbing any sediment which may lodge on the bottom of the chambers.

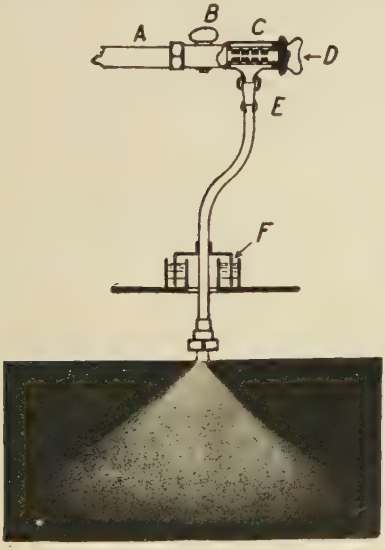


FIG. 87.

Supply of Water. The steam inlets to the chambers or water sprays, as the case may be, preferably the latter, are located along the top of the chamber, and the connections are sometimes carried down to index valves located on the working floor or on a working gallery according to the preference of the designer. If water sprays are used they are preferably located on the top of the chamber, 15 to 30 ft. apart, and staggered. No spray should be used at the beginning of the first chamber where the ample supply of moisture from the Glover is available. Connections may be provided for the last chamber but would rarely be used. Steam is often preferable in the last chamber to sustain the temperature. In some cases special water pumps and storage vessels are used, but the source of supply depends largely on local conditions. In all cases, however, the water should be well filtered in a general filter, and in addition a small lead strainer provided with the finest brass wire gauze should be inserted in the water supply line right next to the spray nozzle. The water-luted method of connecting sprays into the top of the chambers is shown in Fig. 87, which illustrates an acid-proof spray[1] in position. *A* is the water supply line, *B* the

[1] Made by Schutte & Koerting Co., 12th and Thompson Sts., Philadelphia, Pa.

shut-off cock, *C* the filter cylinder, *D* the removable plug for filter when cleaning, and *E* the lead pipe water-luted at *F* and easily removable.

Draft. It has been shown that a certain time is required to complete the reaction to the point when the remaining gases may safely be introduced into the Gay-Lussac, that a sudden increase of draft upsets the operation of absorption and leads perhaps to loss of niter, that a sudden decrease leads to absence of SO_2 and niter or relative excess of moisture and fixation of niter in the last chamber, and that either change of draft leads to variation in composition of burner gases. In order to better overcome the variations of wind pressure and barometric pressure and reduce the operation of the chambers to a smooth and even process variable by intention only, the regulation of draft is of the utmost importance. For this purpose an automatic regulator is generally located either between the last chamber (or tower) and the Gay-Lussac, or at the exit of the Gay-Lussac.

Special Chambers. Certain special chambers deserve mention and comment. Theodore Meyer utilizes the centrifugal action of gases introduced tangentially into a circular chamber to separate the converted gases from those which have not undergone conversion, the temperature of which has not thereby been raised. The circuitous path, it is claimed, insures better exposure of every particle of gas for a longer period to the action of the nitrous vapors. Fig. 88, Plan No. 2, illustrates the arrangement. Several are in satisfactory operation in the United States and a number abroad, but the writer does not happen to know of any that are doing phenomenal work.

F. J. Falding's invention is described as an apparatus for making sulphuric acid consisting of one lead chamber higher than it is long or wide, combined with a Glover tower, means for cooling the reaction products from the chamber and a Gay-Lussac tower. J. B. F. Herreschoff has for fifteen years been advocating the advantages of chambers considerably higher than their width, pointing out that the construction of roof and foundation were substantially the same for any height and that it was the sides and not the top of the chamber which gave most efficient cooling. Great credit is due Falding for his pioneering, even though in no instance does this chamber appear to have achieved phenomenal intensity or economy. It is claimed that, " in the improved lead chambers, the hot gases ascend by convection to the top of the chambers, whereas the lower zone is relatively cold and the mixture of gases may be drawn off from the bottom of the single chamber with the reaction practically quantitatively complete." Fig. 88 gives some extremely good details for attachment of chambers to structural steel frames, together with general elevation and plan of Falding's chamber (elevation 1 and plan 1) as compared with Meyer's tangent system (plan 2 and elevation 2), and with the ordinary style of chambers (plan 3 and elevation 3). The largest chambers in the world were built on this system at Copperhill,

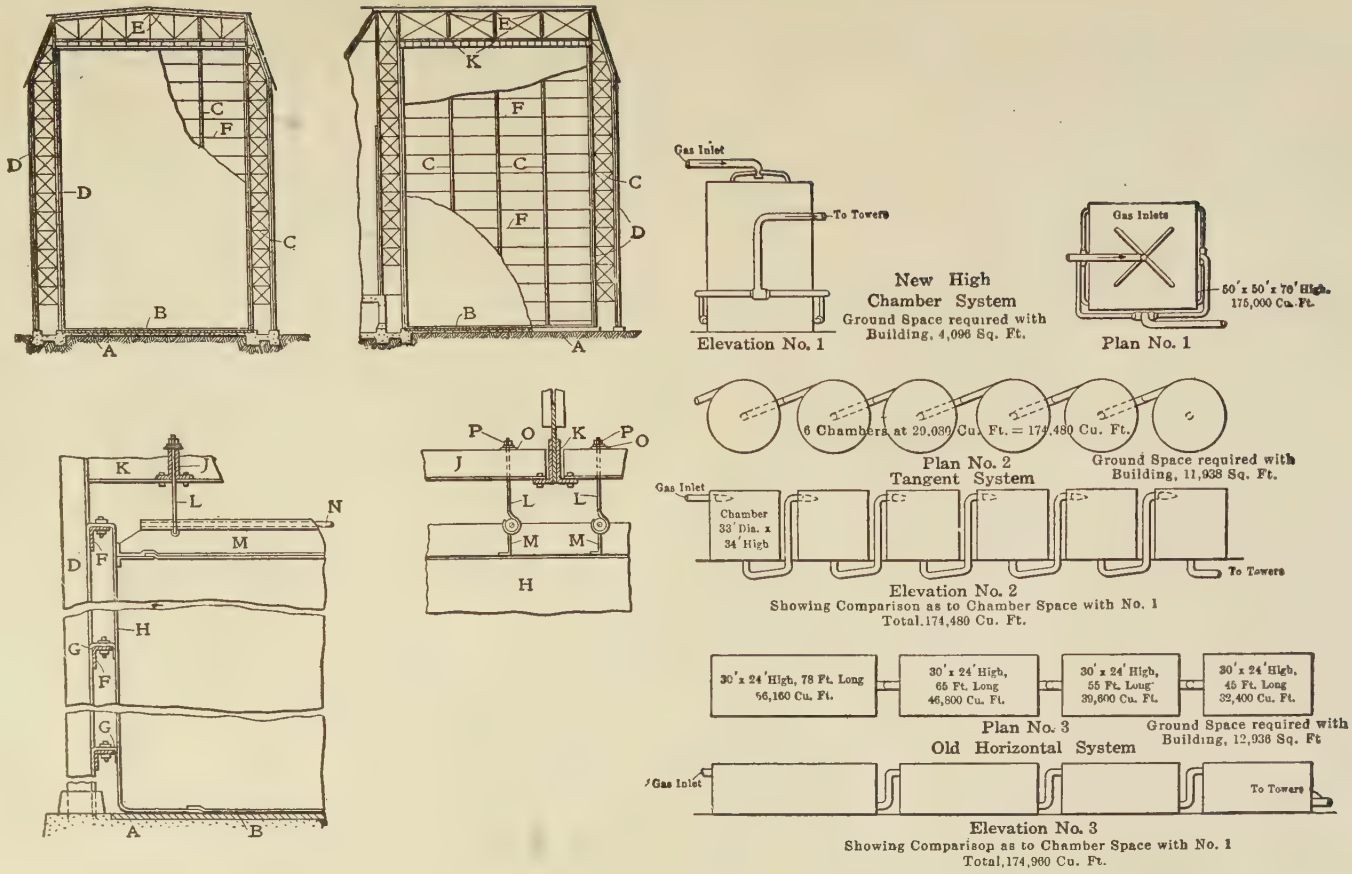

E
C
F
D
D
C
B
A
E
K
F
C
C
C
F
D
B
A
Gas Inlet
To Towers
Elevation No. 1
New High
Chamber System
Ground Space required with
Building, 4,096 Sq. Ft.
Gas Inlets
50′ x 50′ x 70′ High.
175,000 Cu. Ft.
Plan No. 1
6 Chambers at 29,080 Cu. Ft. = 174,480 Cu. Ft.
Plan No. 2
Tangent System
Ground Space required with
Building, 11,938 Sq. Ft.
Gas Inlet
Chamber
33′ Dia. x
34′ High
To Towers
Elevation No. 2
Showing Comparison as to Chamber Space with No. 1
Total 174,480 Cu. Ft.
30′ x 24′ High, 78 Ft. Long
56,160 Cu. Ft.
30′ x 24′ High,
65 Ft. Long
46,800 Cu. Ft.
30′ x 24′ High,
55 Ft. Long
39,600 Cu. Ft.
30′ x 24′ High,
45 Ft. Long
32,400 Cu. Ft.
Plan No. 3
Old Horizontal System
Ground Space required with
Building, 12,936 Sq. Ft
Gas Inlet
To Towers
Elevation No. 3
Showing Comparisop as to Chamber Space with No. 1
Total, 174,960 Cu. Ft.
K
L
N
M
D
F
H
G
F
G
A
B
P
O
K
P
O
J
L
L
M
M
H

FIG. 88.

Tenn., for the Tennessee Copper Co. A view of this plant is given, Fig. 86. The single chamber effect, however, is subject to too quick variations and consequent disturbance of condition, and does not seem to give better action in any respect.

Niter Recovery. The Gay-Lussac tower should next be considered, for in it as much as possible of the oxides of nitrogen must be absorbed in sulphuric of not less than 60° Bé. in order that they may be returned to the system by dilution and heat in the Glover tower. As the nitrous vitriol supplies about 90 per cent of the niter used in the process, it is obvious that proper means for the recovery of the niter is essential. It has been seen that a reduction in the amount of niter supplied by the Glover quickly reduces the rate of conversion and the temperature in the chambers, that if too much SO_2 and moisture are permitted to reach the last chamber, a reaction occurs that tends to tie up niter as HNO_3 in the bottom acid there and that the resulting gases go to the Gay-Lussac poorer in niter, too rich in SO_2 and moisture, thus tending to denitrify the outflowing acid. Not only does this tend to disturb the action of the Gay-Lussac, but it tends to weaken the nitrous supply going to the Glover and further reduces the supply to the chambers. The disturbance is, therefore, cumulative. It is counteracted in two ways. Two Gay-Lussac towers are used in series and the flow on the first is made a recirculated flow much heavier than the supply of fresh acid to the succeeding tower or of nitrous vitriol to the Glover. The effect is proportionally lessened. Also a considerable depth of bottom acid is carried in the chambers at about the strength when slight dilution rapidly liberates niter. Not only does the increased mass of this acid serve as a balance wheel, its higher vapor pressure of N_2O_3 supplying niter to the chamber gases when their partial pressure is low, but it also acts as a direct corrective whenever by lack of niter the drips become weak and slightly dilute the bottom acid. Too much emphasis, however, cannot be laid on the smooth and even regulation of the niter supply. One of the objections to potting of niter is that the action is somewhat irregular, whereas nitric acid run into the Glover tower along with the nitrous vitriol can be regularly supplied and instantly adjusted. Similarly the first step toward avoiding trouble is to provide the chambers with an ample stock of niter rapidly and repeatedly renewed by providing them with ample Glover capacity and large Gay-Lussacs.

Dimensions of Gay-Lussac. The dimensions of the Gay-Lussac tower necessarily correspond in a measure with those of the chamber and with the capacity of the burners as well as the method of operation. Intensive working naturally requires the larger Gay-Lussac capacity. One per cent of the total chamber space may be sufficient for English practice of 22 cu.ft. to 29 cu.ft per pound of sulphur. Two per cent Gay-Lussac space may suffice for the American practice of 16 cu.ft. to 22 cu.ft. per pound, but 3 per cent of the chamber space is almost necessarily required for intensive working on the basis of less than 16 cu.ft. per

pound. As a matter of fact it would be economy in the long run to use not less than 2 per cent in any case and 3 per cent if the method of operating the chambers is to be more intensive than 20 cu.ft. per pound of sulphur. These percentages apply to the space occupied by the packing and its interstices and not to the total space within the lead shell.

Gay-Lussac Packing. The packing of the Gay-Lussac may consist of coke, but it is probably true that the best grades of coke occasion a considerable loss of niter. Tile or special earthenware shapes are widely employed and the greatest advantages are claimed for them, but in all probability pumice on the whole gives the best result and only its expense is against it. Whether coke, pumice or stoneware is used the greatest care should be used in its selection. Laboratory tests are not satisfactory for this purpose and experience with the character of the material in actual tower service should be the only guide to its selection. As with the Glover tower, the supply of acid to the Gay-Lussac should be as regular and evenly distributed over the entire cross-section as possible. With the Gay-Lussac, however, we have only one kind of acid to supply. The same luting principle is used, only the cups are not alternately supplied with a different kind of acid. From the Gay-Lussac the gases are generally allowed to exit directly to the atmosphere or to some large stack if one having the needed spare capacity is at hand. Lunge states that the Gay-Lussac towers need not be lined as are the Glovers. They need not be, but it is frequently considered to be in the long run economical to protect the Gay-Lussac towers from possible mechanical injury and from immediate contact with the gases by a thin lining of a single wall approximately $9\frac{1}{2}$ ins. Some space is thus sacrificed, but in the larger towers constructed these days the proportion of this space is relatively small.

The higher towers require horizontal joints in the lead sheets which cannot generally be obtained long enough to reach to the bottom of the tower. These joints should always be made by lapping and burning on the outside with the lap hanging down on the inside. None of the main vertical joints should be near a corner. The changes of temperature in the Gay-Lussac tower are said to be less than those in the Glover and it is generally stated that the Gay-Lussac sides may well be burned to the bottom pan. As a matter of fact, however, in a properly lined Glover the temperature of the lead shell is not greatly above that of the atmosphere and the range of variation of the lead itself is approximately the same in the Gay-Lussac and Glover. There seems to be no good reason for changing the construction in this respect. A similar framework (except higher and therefore stronger) and similar methods of attaching the sides to the framework are used with the Gay-Lussac that have been described for the Glover.

Circulating System. It is now proper to desribe in more detail the acid circulating system and the apparatus provided for this purpose. It will be apparent that large quantities of acid have to be elevated to the

tops of the towers. Calculation shows that the nitrous gases for their sufficient recovery require that an amount of 60° Bé., equivalent to 60 per cent of the total production of the chambers, be run down the Gay-Lussac per day. In practice this is generally 90 to 150 per cent. When intensive work is used, 150 to 300 per cent is needed. The practical limit is sometimes introduced by the heating and concentrating capacity of the Glover. The denitrating action of the Glover, however, is very largely dependent on direct action of SO_2 (importance of having rich hot gases) and, if the chamber acid is otherwise concentrated or is used up in the works, or is sold, and the Glover acts mainly if not wholly as a denitrator, this concentrating limit is not so quickly felt. The Glover product must be always about 60° (77.6 per cent) or the absorption in the Gay-Lussac will be unsatisfactory. The chamber acid will not much exceed 53° Bé. (69.66 per cent) and the mixture of acids at the head of the Glover should not be stronger then 58° Bé. (74.36 per cent), preferably less, if it is to be fully denitrated and niter is not to be lost as an impurity with 60° acid shipped or used. This 58° would permit (for the concentration in the Glover of the entire "make" of chamber acid) the admixture of two times this

Fig. 89.

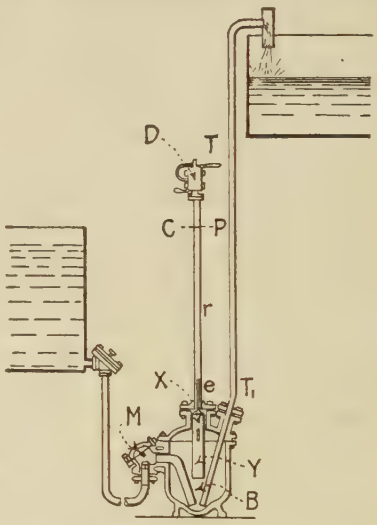


Fig. 90.—Kestner Automatic Elevator.

"make" from the Gay-Lussac. Twenty tons 60° acid made per day would thus require 40 tons for the Gay-Lussac and the elevation of 100 tons to the heads of the towers if a single Gay-Lussac were used. Two Gay-Lussacs would mean the elevation of more than 140 tons per day.

This lifting has almost universally been done by compressed air admitted into vessels, Fig. 89. These "eggs" are filled with acid through a pipe containing some form of check valve that prevents its return. Air is then automatically or manually admitted through another pipe. A third pipe from the bottom of the vessel permits the acid under pressure to leave the vessel followed by the rush of air of equal or slightly greater compressed volume than the acid pumped—a method wasteful in the extreme. Fig. 90 shows one of the automatic Kestner lifts attached to a small acid egg, the operation of which will be apparent from the

illustration. These Kestner lifts have been used for years by many of the largest acid manufacturers and have given entire satisfaction.[1] Moderately heavy walled lead pipe is used throughout the chamber plant for the transportation of acid. Recently lead-lined iron pipe has found great favor for that portion of the acid lines subjected to very heavy pressure (like those from the eggs to the heads of the Gay-Lussac tower) or to jars by reciprocating pumps or lifts. Geared pumps if made of iron require excessive repairs. Stoneware pumps have not this objection, but are hardly safe to use above 30 lbs. pressure or 40 ft. acid-head. Centrifugal pumps, arranged in stages, have been tried with excellent success for low lifts of strong acid, but in the chamber work all of the acid is 62° or weaker and the necessity for perfect regularity of operation makes it undesirable to multiply the mechanical devices necessary to accomplish the single lift. Positive acting steam pumps have been used successfully for acid, but are corroded and it is doubtful whether they are any more economical than the best air lifts (Pohlé) where the necessary depth is obtainable. Figs. 91, 92, and 93 show the general arrangement of three different types. Pohlé lifts consume only about half the air required for blowing by eggs, furnish a steady stream like a pump, are without moving parts and can be made practically free from wear. For small installations they are very satisfactory even for lifting by stages when the necessary depth can be obtained without too much expense. *A* is the air pipe through which compressed air is carried down to the bottom of a well or shell surrounding the pump pipes. *B* is an acid pipe connected with the tank supplying acid to be elevated. *C* is the pipe for carrying the mixed air and acid up to the point of delivery. The distance from the bottom

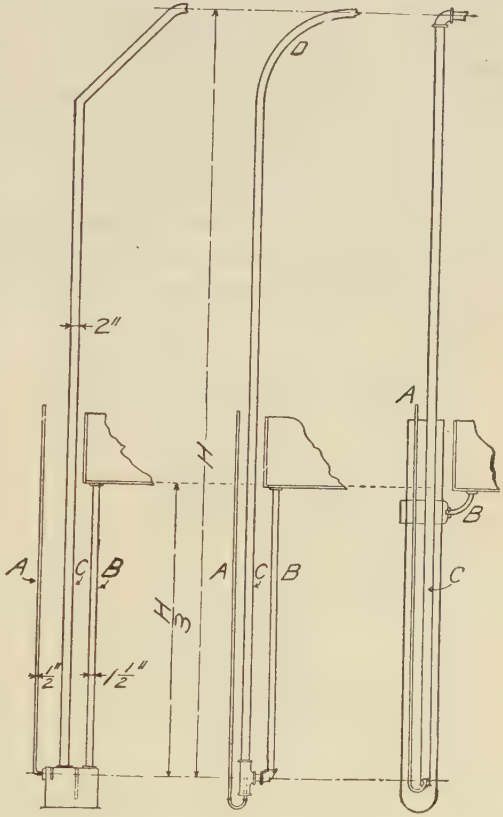


Fig. 91. Fig. 92. Fig. 93.

[1] They may be obtained from the Bethlehem Foundry and Machine Co. complete with all accessories.

of the acid tank to the bottom of the well or point of emission of air should be at least one-half of the lift from the tank to the point of delivery. The three different arrangements are substantially the same in general effect but Fig. 93 is to be preferred because by this arrangement it is possible to get at and remove either the air pipe or the acid supply or the lifting pipe without affecting the general arrangement of the whole apparatus. Also at the head of the air lift long curves (*D*, Fig. 92) should be used rather than angles since the shock of the alternate plugs of air and heavy acid frequently causes sufficient jarring to injure the pipe.[1]

Movement of Gases. The fans used for actuating the gases in the chamber system are of three types, according to location, between the dust chambers and the Glover, between the Glover and the acid chambers, or between the acid chambers and the Gay-Lussac.

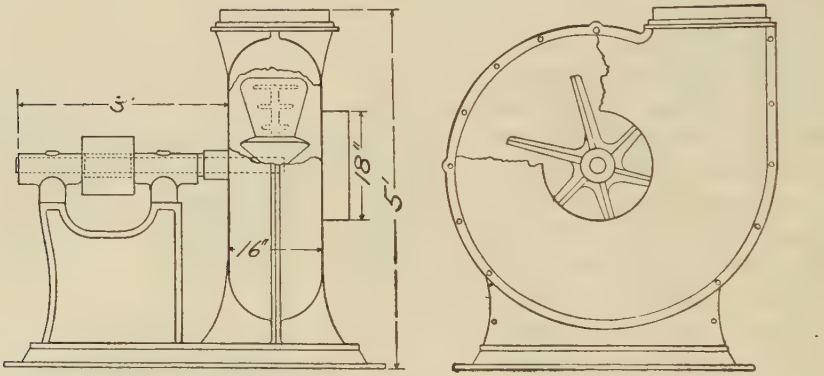


Fig. 94.

In the first case a steel fan,[2] water cooled, is used very successfully in handling the hot gases; in the second place a regulus metal fan [3] is frequently used as that illustrated in Fig. 94, and in the third instance a stoneware fan [4] may be used such as is illustrated in Fig. 95. Stoneware fans may possibly be used between the Glover and the first chamber, but the high temperature is exceedingly liable to cause breakage of a fan

[1] The quantity of acid handled in a large sulphuric acid plant operating on the intensive system, is very great indeed, reaching in some instances 6000 tons a day. Elevation of this acid by the old blowing method would be subject to an almost prohibitive expense, particularly in view of the higher Gay-Lussac towers and the larger general scale of commercial operation. So far the best method of elevating large quantities of acid in the chamber system is that employed by Utley Wedge. This consists of balanced steel mine skips attached to a cable running over a hoisting drum located above the heads of the towers or in an adjacent hoisting house.

[2] Manufactured by A. P. O'Brien, Richmond, Va.

[3] Manufactured by the Sturtevant Blower Co., of Hyde Park, Mass.

[4] The particular fan is selected from the patterns of the Didier-March Co., New York City.

blade or of the entire blast wheel. Running at such high speed any break might cause very serious damage to the lead flues, or chambers, or both. On the other hand, the regulus metal fan (owing to the heat, velocity and considerable niter content of the gases) is subject to rapid corrosion. Such a fan may also be used between the chamber and the Gay-Lussac but, in this case, there is no objection to using the stoneware fan which is entirely practical and absolutely permanent. In the writer's opinion, where only one fan is used it is best located between the burners (or else the dust chambers) and the Glover tower, and constructed on the O'Brien principle. Extremely satisfactory results have been obtained in this way. Where this is objectionable or where it is desired to operate with a balanced draft (two fans) as recommended by Falding, the second fan can best be located just before the Gay-Lussac tower. For this purpose the writer prefers the larger sizes of stoneware fans.

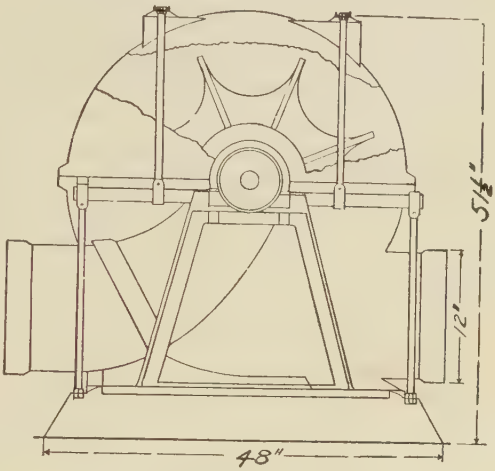


FIG. 95.

Steam jets, formerly considered so valuable, are an extremely expensive means of securing draft and should only be used in case of emergency for which purpose they are best located at the exit of the Gay-Lussac tower. Beyond question, however, much can be done to reduce the amount of power necessary to secure a good draft (if not eliminate mechanical draft entirely) by judicious selection of flue cross-sections and of relative heights of inlets and outlets.

This is particularly the case where the ground configuration permits location of apparatus at very different levels without the building of expensive supports and foundations. When the Glover is located well above the burners, the chambers set high above the ground, when a tall Gay-Lussac is used and open packing employed for these towers with large connecting flues, natural draft is generally found to be sufficient for "moderate" working. "Intensive" working with narrower chambers, intermediate towers, larger percentage of niter to be recovered and two Gay-Lussacs more closely packed, requires forced draft. The use of fines burners and efficient dust chambers further adds to the resistance in the path of the gases.

Purification of Sulphuric Acid. Sulphuric acid as manufactured in

the chambers, particularly as concentrated in the Glover tower, exhibits certain impurities that are quite important from an industrial point of view. These are lead, iron, arsenic, selenium, antimony, aluminum salts, nitrous oxides and nitric acid, platinum, mercury, the alkalies, calcium, and copper. Most of these impurities can be traced directly to flue dust and experiments carried out during the development of the contact process indicate that practically all of these impurities can be removed by filtration provided other reasons justify sufficient cooling to permit thorough filtration before passing to the chambers. Unfortunately, this prevents the use of a Glover because the gases cannot be satisfactorily filtered unless they are cooler than 200° C. Much, however, can be done to reduce the amount of these impurities by the thorough removal of dust.

Where pure acid is required, however, none of these preliminary means will serve. The acid must be treated specially in order to obtain the desired results. It is found that if the acid is treated with H_2S for the removal of arsenic, practically all other impurities are removed at the same time and the acid is even clarified from some inert suspended matters that are undesirable in appearance only. If, however, a thoroughly pure and limpid acid is required, there is practically no way of obtaining it except by distillation on the one hand or the use of the contact system on the other. Sulphuric acid as made in the chambers will vary in its arsenic content from about 0.1 per cent up to about 0.3 per cent according to the ore used and the amount of dust carried over from the burners.

Where concentrated acid along with battery acid is to be made by the Herreschoff system the easiest way of disposing of arsenic is probably to oxidize it thoroughly with nitric acid and heat, after which the excess of nitric is removed with ammonium sulphate. As, however, the use of the Herreschoff system of concentration is exceedingly limited, two general methods of purifying are most common, both depending upon the action of sulphides liberating H_2S. As acid of 55° Bé. acts directly on the H_2S, decomposing it and giving off sulphur that is extremely difficult to remove by filtration, it is best in carrying out the purification of the acid to have it diluted to about 45° or 48° Bé. Herein lies the chief objection to the chamber process for the making of pure acid. The chamber process should concentrate substantially the entire make to at least 60° Bé. by use of the Glover tower, simultaneously denitrating all the nitrous vitriol from the Gay-Lussac. If purified acid is required, this concentrated acid from the Glover must be diluted with considerable quantities of water or else the chamber acid must be taken and slightly diluted for the purpose. Then after purification it is practically impossible to concentrate the purified acid by the heat of the Glover tower, even when carrying out the nitration in another Glover, without so far causing the contamination of the acid as to undo all that has been done by purification. This explains why many works manu-

facturing acid for the general trade have so long retained the old system of purifying acid direct from the chambers and then concentrating it above the burners and finally in platinum stills. Likewise it explains the great progress made by the contact process with manufacturers whose output is distributed widely to the general chemical trade.

After the sulphuric acid has been diluted to the necessary strength, it is submitted to the action of substances producing hydrogen sulphide, or to the action of the gas itself, in large tanks arranged for alternate precipitation and intermediate settling of the arsenic sulphide produced and likewise arranged to be connected alternately with filter tanks where the last traces of this mud can be separated out from the acid. The method most generally used in this country is believed to be the purification by means of gaseous H_2S. This is prepared by the action of sulphuric acid on ferrous sulphide in a heavily built generator, similar in principle to the Kipp.

The hydrogen sulphide gas is supplied to the acid in either of two ways, tanks or towers. The objection raised to the former is that the gas has to be pumped through such a considerable depth of liquid; this seems unimportant when it is considered that it only means making the generator somewhat more resistant to pressure and arranging the gas pipes so that they can be elevated nearer to the surface, when the gas generation is substantially over, to let the residual gas out of the generator. If towers are used, the acid is distributed to their tops in very much the usual way and they are carefully packed with shaped stoneware or brick pieces of approximately triangular section so that no flat upper surface can be presented for the collection of the precipitate. Slight pressure is sometimes used in the tower and generally the exit gases are scrubbed with water or milk of lime to retain any H_2S that might otherwise pass away. The test used to ascertain when purification has been sufficiently complete is the ordinary Marsh test. The acid running down out of the tower is yellow in color and extremely muddy. Sometimes part of the arsenic sulphide is removed by preliminary settling. Others take the entire mud directly to the filter tanks, false-bottom tanks with grid composed of heavy plank covered with lead or acid-proof brick having communicating gutters underneath. In either case the grid is covered first with pieces of quartz and then with finer material until the grade of ordinary sand is reached over which is a perforated lead sheet to prevent disturbing the sand when the arsenic sulphide is removed. The filtering layer thus formed is finally covered with a layer of arsenic sulphide dry. The acid is run in carefully, not to disturb this layer, and then the level of acid maintained without allowing it to reach the surface of the filter until it is found necessary to empty the filter entirely to clean it. The period for cleaning such a filter is approximately one to five weeks according to the quantity and impurity of the acid used. From the bottom of the tank a down-flow pipe passes into a liquid separator to which

suction is applied and out of the bottom of which the acid flows into a liquid lute provided in a tank from 12 to 18 ft. below according to the suction to be used.

A better practice in precipitating the arsenic sulphide is to use separate tanks for the precipitation from those used for filtration and also a final absorption tower. The precipitation tanks are provided with steam pipes for heating and with perforated pipes for introducing the H_2S. The latter are connected from a general H_2S main leading to the generator. Each tank is covered and has a pipe for the unabsorbed H_2S which leads it to a small absorbing tower. Down this tower is run a stream of acid just sufficient to supply the capacity of the purification plant. That is, while one tank is being treated another is being filled by the slow stream of acid from the tower and the rate of filling of the second tank is so regulated that it is ready to treat by the time the other tank is ready to be filled. A set of filter tanks is provided on a considerably lower level. Unlike the usual filter tank these have a large compartment below the filter bed into which the acid is conducted from the tanks above so that the filtration takes place upward through the bed, and clear acid appears above and can be syphoned off at the convenience of the operator. In the precipitating tanks, the treatment can be so arranged as to allow a considerable period for settling and part of the acid can then be drawn off from the upper tanks directly into the upper compartment of the filter tanks sufficiently clear for practical purposes. The advantage of filtration from the bottom upward is that when the filters finally become clogged it is not necessary to dismantle them or remove any of the material. Instead the mud is drawn from the bottom compartment along with some acid into a settling tank from which the clearest acid can be returned for filtration. The outlet from the lower compartment is then switched to a storage tank used for preparing dilute acid for the hydrogen sulphide generator and the water hose is turned into the upper compartment above the filter. The passage of water downward through the filter carries backward out of the interstices all the accumulated arsenic sulphide and leaves the filter substantially clean and ready to start in again on a new cycle.

By this means sulphuric acid containing a total impurity of .05 per cent can readily be obtained. The arsenic is substantially eliminated if the treatment is carried out with gaseous H_2S, falling to about .003 per cent. For comparison it may be noted that the best contact acid contains about .000005 per cent.

Of the various methods used for the precipitation of the arsenic and other impurities by generation of the H_2S within the liquid, probably the best, and certainly the most frequently used, has been the precipitation with barium sulphide. The advantages presented by barium sulphide are two-fold. First, the barium itself is precipitated as sulphate in the liquor and adds greatly to the weight and density of the precipitate.

Second, substantially no soluble material is left in the liquor to interfere with subsequent concentration or use of the acid. The acid, however, must be diluted to sp. gr. 1.4 containing 50 per cent of H_2SO_4. To obtain the best results it must then be heated to about 80° C. and a warm solution of barium sulphide $7\frac{1}{2}$° to 8° Bé. run in at the bottom of the vessel in such a manner as to prevent the escape of H_2S. The most convenient way of doing this is to divide the liquid through as many small openings as will permit the passage of the gas without plugging up by formation of the precipitate. These openings may profitably be placed beneath a perforated shelf of lead, or a ribbed shelf without perforations but around the edges of which are serrations to divide the bubbles of gas again. The separation of the purified liquid from the mud may be carried out by either of the usual filtration methods. The only objection presented by the barium sulphide treatment is that the purification cannot be carried so far in this way. Nearly double the amount of arsenic remains in the acid. This can, of course, be removed by subsequent treatment with gaseous H_2S, but if the treatment by gas is to be undertaken, the whole operation might better be carried out by the gaseous method.

The Concentration of Sulphuric Acid. Two systems of concentration, illustrating the wide range of principles employed in practice, will be described.

The first installation, Figs. 96 and 97, will be that likely to be found in a chemical plant manufacturing a good grade of 66° acid; according to methods at the disposal of one who does not control or care to pay royalty upon contact processes. The acid will have been purified in some manner, probably by the use of H_2S gas, and will be approximately 46° Bé. Lump burners will be found of the usual type except that probably the flue above the arches will be somewhat higher at one end.

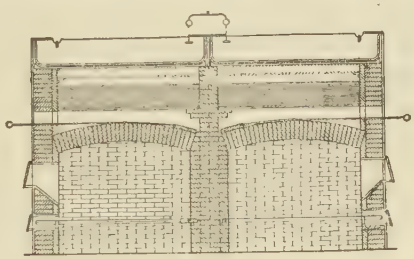


Fig. 96.

The common flue above the burner is crossed at suitable intervals with supporting beams, set in reinforced concrete. Beginning with the burner furthest away from the supply of acid, the flue is very low, increasing in height toward the acid supply end. This results from the successive rise of the lead pans to allow for the downward flow of the acid. Upon these protected I-beams are laid cast-iron plates, $1\frac{3}{4}$ ins. thick at the lower end and 1 in. at the upper end furthest away from the burner arch. Passing backward along the flow of the acid each of the beams is raised 1 in. higher than the preceding. On the iron plates a layer of coarse sand is placed, as thin as can be made with absolute certainty of everywhere having a separation of sand between the iron and lead in order to prevent

immediate contact between them, as these points would thus become overheated and cause excessive corrosion of the lead. Two or three layers of thin asbestos paper may be used instead of the sand. The pans vary gradually in depth from 8 to 14 ins. and vary also in thickness, from 25 to 10 lb. lead being used. After the pans are all in place the long double edges where they abut, are bent over to form lips. The direct flowing of the acid over these lips is not altogether desirable, first because it wears the lip, and second because the 2 ins. left below the top of the pan does not give a sufficient factor of safety in case of temporary obstruction to the flow. For the transfer of the acid under ordinary circumstances, therefore, a small syphon hung in this lip is preferred.

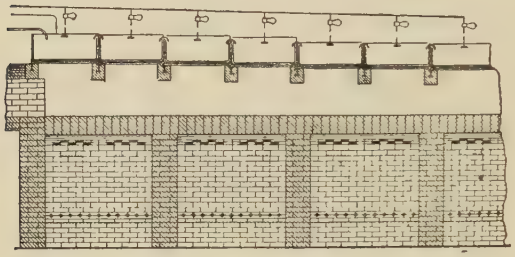


Fig. 97.

From the series of pans, Fig. 97, the acid continues its downward flow into another series of pans, which may immediately adjoin the first series or be located in an entirely different building. These pans utilize the waste heat from the higher concentration apparatus to be described, and are located over the flue supported on perforated cast-iron plates. These plates give a larger output with entire safety and better fuel economy, but do not serve to protect the flue below as do the solid plates rimmed around the edge. The acid then flows from the pan to the platinum still, the rate of flow being regulated automatically.

Platinum Stills. Many shapes and patterns of platinum stills have been designed and special advantages claimed for each. In all probability the net result is just about the same in the long run except that the lower and longer pans are more economical of platinum. Some stills are provided with baffle partitions causing a circuitous flow of the acid through the still, the advantage claimed for these being that a better concentration is obtained in a single operation. Against this must be set, not only the small increase in platinum, but also the very great increase in liability to leakage and in irregular strains on the bottom of the pan. Corrugated bottoms are used in some patterns of platinum still. They present about 60 per cent more surface for transfer of heat, but on the other hand, increase to some extent the difficulty of making side joints and consequently the liability to leakage. They have, however, the advantage of stiffening the bottom. Lining with gold has been found to greatly increase the life of the platinum pan and, at the present relative prices of gold and platinum, is a very marked saving. Gold resists about seven times as well as platinum. The gold is not plated on or attached by

dipping, but must be attached by the method invented by one of Heraeus's assistants. The overheated gold is poured on top of the platinum ingot heated nearly to fusion, forming a double ingot which is then rolled into the sheet to be made up into stills.

The chief agents injurious to the stills are the hydrogen, carbon, sulphur and silica (from the fire gases, causing crystallization and brittleness of the platinum), or mercury (forming amalgam) or iron and aluminum sulphate with traces of calcium sulphate, magnesium sulphate, lead sulphate and silica (from the acid in the stills, forming crusts and tending to cause local overheating, undue mechanical strain, and possibly chemical injury).

A pair of stills which with accessories weighs about 100 lbs. and cost $75,000 in 1913, now would cost about $150,000.

The prohibitive cost of platinum ($105 per oz.) makes it temporarily obsolete. Better designed stills with tile lining, Kestner stills, towers, or silica dishes in cascade are rapidly replacing it.

Where concentration of sulphuric acid is to be carried out, it is often found to be desirable to remove the last traces of lower oxides of nitrogen. This is best done by addition of ammonium sulphate, liberating the nitrogen as such. Nitrosyl sulphuric acid reacts with ammonium sulphate as follows: $2NO_2HOSO_2+(NH_4)_2SO_4=3H_2SO_4+2H_2O+4N$. With N_2O_3 the reaction is $N_2O_3+2NH_3=3H_2O+4N$. With nitric acid, $3HNO_3+5NH_3=9H_2O+8N$. Ordinarily about .1 to .5 per cent of ammonium sulphate is required. It has been found that, while the reaction of nitrosyl-sulphuric and N_2O_3 is rapid, with nitric it is slow. Therefore the presence of nitric acid in sulphuric to be concentrated nitrous-free should be as far as possible avoided and as an added precaution it is well to add the ammonium sulphate far enough in advance that it may have ample chance to be heated and boiled with the acid for a considerable time before passing to the still. This is most conveniently carried out in the present installation by the addition of the ammonium sulphate to one of the earlier pans. Of course where purified acid is being treated, as in the particular installation described, the addition of ammonium sulphate will hardly be necessary.

What has been for many years regarded by some as the most perfect type of concentrating apparatus for sulphuric acid, is the still or furnace which was invented by Mr. L. Kessler, securing from the French National Society for the Encouragement of Industry the first gold metal. Since its original development in 1890 the apparatus has been improved in minor details, but it is substantially the same and still remains one of the best for the concentration of sulphuric acid that has ever been developed. Fig. 98 shows the arrangement of the Kessler apparatus. Fig. 99 and 100 is a detail of the portion in which the hot gases first come in contact with the acid, and also of that portion of the apparatus in which the preliminary concentration is carried out. In C, Fig. 98, a deep coke fire

is built, making it practically a coke producer-gas installation, and ports are provided above the fire for the admission of a regulated supply of excess oxygen for burning the carbon monoxide produced in the coke fire. An excess of this oxygen is allowed so as to somewhat reduce the temperature of the gas and the heated gases are taken through the flue into the saturex at about 900° C. The first apparatus is called the gasogen or gas-making apparatus. It is built entirely of brick properly buck-stayed, provided with a simple and convenient grate and an opening in the top for supply of coke. The fire is built so that it requires attention not more than twice during the twenty-four hours and sometimes only once in twenty-four hours. During this period of replenishing the fire a damper permits entire shutting off from the concentrating apparatus so that any dust formed during this period of disturbing the fire is not carried into the acid. The duration of this interruption does not exceed one hour, and with proper equipment may be completed in half an hour or less, the larger part of this time being given to clearing the fire of dust by allowing it to burn directly up the stack for a few minutes. After the gases above the fire have become clear, the damper is opened and the heated gases admitted directly to the saturex.

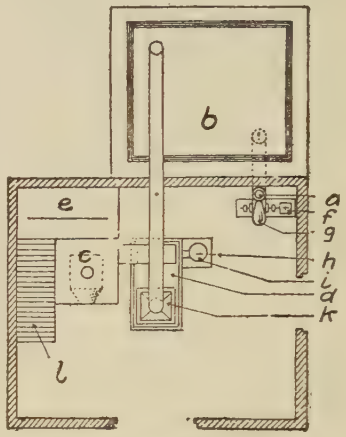


FIG. 98.

The saturex in which the final concentration is carried out consists of a volvic lava box carefully fitted and joined with acid cement, surrounded by a packing of extremely fine quartz sand, all of which is encased in lead. Openings to this box with volvic lava plugs are provided at the points *C*, Fig. 99, so that, with considerable ease, the covering plates may be removed, the plugs withdrawn, and any mud which collected in the apparatus taken out. Supported on blocks set in the bottom of the basin, are partitions extending from the top nearly to the surface of the acid. They are so arranged that the gas entering by the flue cannot pass out of the box through the opening in the cover to the plateau or preliminary apparatus, without passing under these partitions. Also they are so arranged as to give the greatest length of narrow opening between the bottom of the partitions and surface of the acid. From here the gases, more or less laden with moisture, and containing some suspended or entrained particles of acid and some anhydride fume, pass upward from the saturex into the plateau. The action of the saturex is not generally well understood. As a matter of fact the gases are not merely blown in a thin stream across the surface of the acid, as is gen-

erally supposed. Instead, when the draft is started, small waves are made upon the surface of the acid which gradually increase until they begin to touch the bottom surface of the curtain. The instant this happens a rather violent agitation takes place accompanied by strong bubbling and splashing of the acid so that the mixture between the acid and the gases is much more thorough than is generally thought. An enormous surface

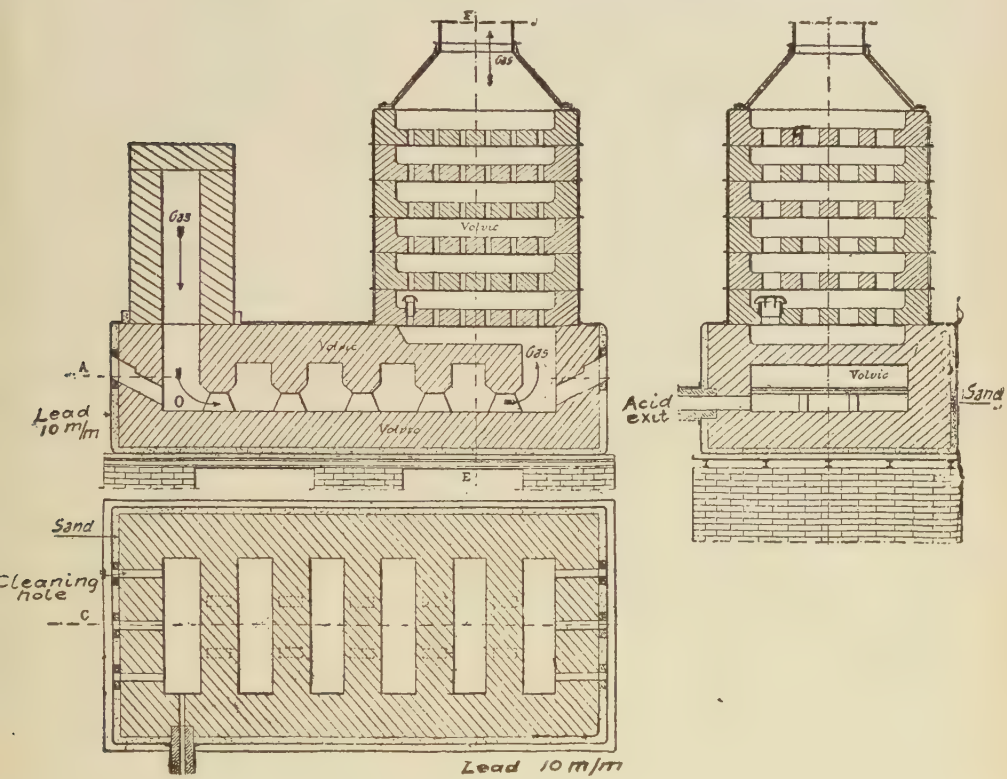
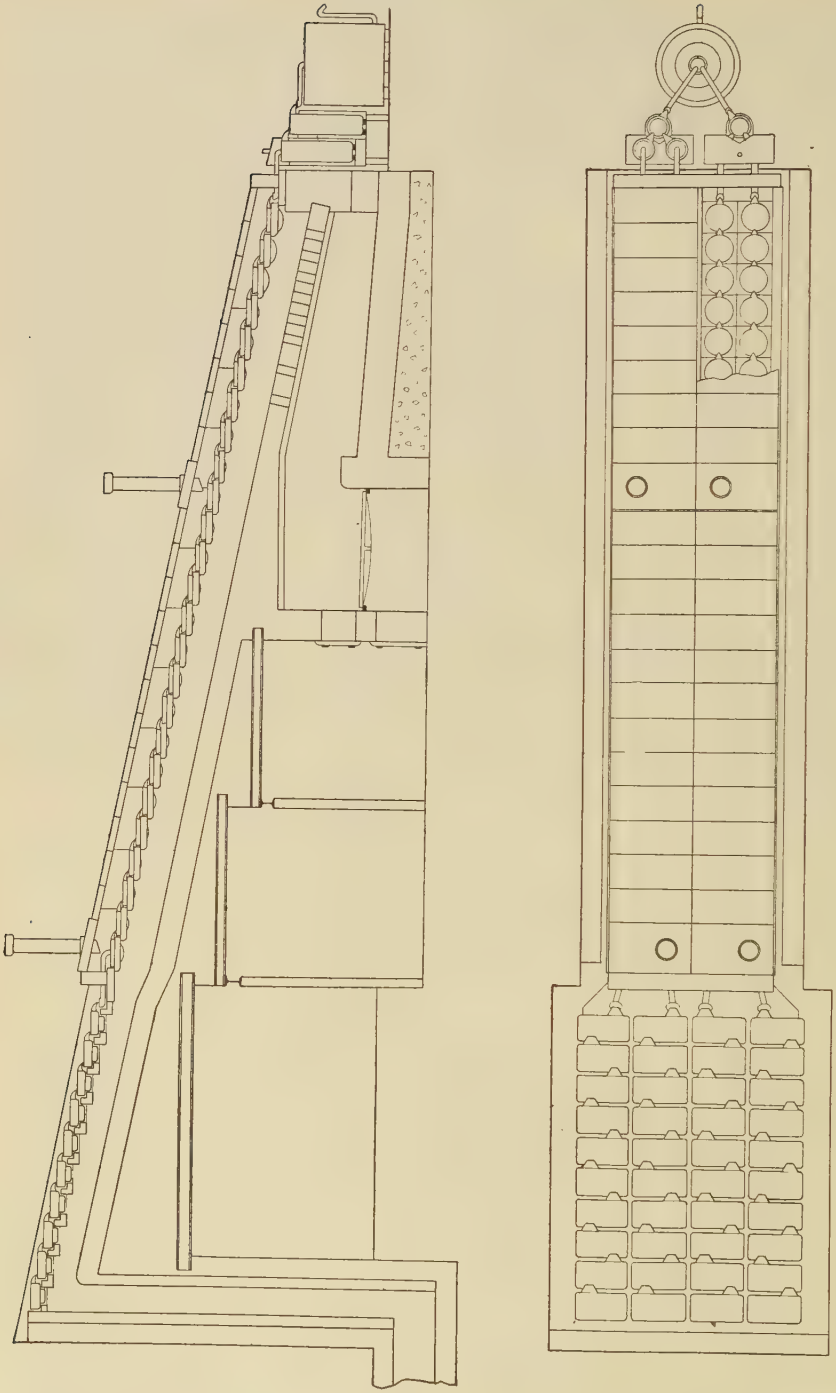


FIG. 99.

is in this way exposed to evaporation by contact with gases of very high temperature. The entrance temperature of the gases approximates 900° C., but the evaporation cools the gases so rapidly that there is very little decomposition of the acid in the saturex. In making 98 per cent that boils at 320° C. concentrated acid leaves the saturex at about 240°. Whatever is decomposed is carried up into the plateau and largely recovered, being brought back with the weaker acid. The process of concentration is really one of drying, almost like a partial vacuum concentration, because the fresh gases are continually blown across the surface of the acid and carry away the water with the gases rather than compelling evaporation into a saturated atmosphere. The temperatures throughout the apparatus are much lower than ordinarily correspond to



Sulphuric Acid Concentrator

Fig. 100.

the concentration made. The ease with which 97 or 98 per cent acid may be made and the small amount of fuel required for that purpose, are marked advantages of this type of concentrating apparatus.

The gases passing up into the plateau carrying much entrained acid, some SO_3, with oxygen and traces of SO_2 from the decomposition of the sulphuric acid below, find their way upward only through certain holes in the plateau or shelves, each of these holes being covered by a calotte or hood having a serrated lower edge. The serrated covers break up the gases passing upward and compel them to bubble up through the layer of acid lying upon the plateau. Evaporation is carried out on five successive levels and dilute acid being fed in at the top of the plateau is rapidly concentrated, at the same time recovering from the uprising gases practically all of the sulphuric acid which they contain and absorbing some of the SO_3. The contact between the gases and the liquid is so thorough that when the gases pass out, their temperature has fallen to about 95° C. From the top of the plateau column the gases are drawn through the flue into the coke box or filter box *b*, Fig. 98. There they are passed downward through a coke bed which rests upon a grilled false bottom composed of iron pipes covered with lead. Herein are caught practically all of the suspended particles of H_2SO_4 which have succeeded in passing the plateau, and a slight amount of SO_3 in its suspended condition which is literally filtered out of the gases.

Following these general principles many tunnels of brickwork with a tall tower packed with quartz have been successfully used for concentrating acid either by hot gases from coke, oil, or even natural gas fires between 1914 and 1917. Some of these have proven unsatisfactory and hasty war construction has caused considerable trouble.

Since the extraordinary war demand for concentrated acid and prohibitive prices of platinum, large numbers of cascade systems have been installed. These consist of a long inclined bench of brickwork supported in part on structural steel and provided under the right-hand end in Fig. 98 with a grate and long fire box for complete combustion of gases. The hot gases then pass up through perforations in the arch into a long flue, the top of which is formed of special tiles having large holes for supporting evaporating dishes of fused quartz (silica ware) or special iron (Tautiron or Duriron). These dishes are generally round over the hottest part of the flue, but may be made square further back without too great danger of breakage. Each dish has an elongated spout out of which the slow stream of acid pours or "cascades" into the dish next below. As the acid becomes more concentrated, it gives off acid fumes and the lower part of the cascade is therefore covered over with large slabs or tiles, four of which are provided with holes connected to pipes of silica and stoneware for carrying off these gases to water-cooled lead condensers. Here the stronger acid may be first condensed and returned with the feeding acid of the system while the aqueous vapor is allowed to pass off entirely.

Such cascades had wholly superseded platinum stills in England even before the war and have done the same here in the last few years for smaller units. Most large units are tunnel and tower systems.

Storage and Packing of Sulphuric Acid. Unless the entire product is to be used at the plant where it is made, it is necessary to store the acid prior to shipment. It is best to store 66°, 98 per cent acid, and oleum in riveted steel tanks generally of large capacity, emptied either through a foot-valve in the bottom surrounded by a low upstand to prevent the drawing of mud, or at various levels through the side, where specially constructed valves having stoneware plugs and seats are used to avoid the gradual leakage that occurs when iron valves are used. As these storage vessels are much too large to permit the application of air pressure for the elevating of the acid, it is customary to locate them on structural steel or concrete supports high enough to run the acid by gravity into cars. It is customary to make these tanks flat bottomed, circular and hemispherically domed. Sometimes lower domes are used to advantage. Horizontal tanks shaped like boilers are used where it is necessary to apply pressure and the storage vessels cannot be elevated to deliver by gravity. For storing acid of 60° Bé. or less, certainly for 50° Bé., lead-lined storage vessels are preferable. These are generally wooden tanks strongly stayed and lined, with 10-lb. lead throughout. In some instances very satisfactory storage vessels have been made by building reinforced concrete tanks, painting the interior of these tanks with pitch and lining the tank with lead. The foot-valve arrangement with porcelain plug and seat can be used in either case. The seat of the valve is set by locating it in place, supported from below by a few strips of wood or similar material, and then pouring in melted sulphur all around it. To make a satisfactory joint great care should be used to have the metallic surface as well as the outside surface of the seat clean and dry and the sulphur should not be too cool. Also the porcelain valve seat should be carefully warmed up so that contact with the hot sulphur does not crack it. These plug valves are operated either by screw stem or by lever. Throughout the works where frequent opening and closing is necessary, and acid distributed through more or less complex lines, asbestos-seated iron plugs or cocks are used with great satisfaction, but should be systematically operated every day. Valves which are not often touched for years and yet which should be ready for emergency service, are much better installed with a stoneware plug and seat in a loose-fitting cast iron socket riveted on the tank bottom.

A blow-off pipe 2 ins. in diameter should be allowed near the center of the tank extending fairly well down away from the manhole plate so that the blast of air which follows blowing the egg into the tank may find free access to the outside atmosphere. Through this pipe a rod or chain may be dropped, or better connected to the float inside the tank and carried over a couple of pulleys to an indicating weight on the outside

of the tank, so that it is practically never necessary to open the tanks in order to ascertain the amount of acid therein and the only occasion for loosening the manhole is the cleaning out of the tank, perhaps once in a year or two. In this manner the corrosion of the interior is very much reduced and the life of the tank greatly increased.

Sulphuric acid is shipped in tank cars, tank wagons, drums and carboys. A tank car is a flat car upon which a steel tank of cylindrical shape is secured on its side by necessary tie rods and end blocks. The capacities of tanks thus used vary from 60,000 lbs. to 160,000 lbs., the thickness of sheet steel used being about $\frac{1}{4}$ in. On the bottom is generally provided a small sump or well into which the " blow-off " pipe dips to empty the tank as completely as possible. Sometimes a foot-valve or cock is provided on the bottom of the tank for emptying, but the better practice is to blow the acid out of the tank with compressed air and to have only a well-bolted flanged nipple on the bottom for cleaning. The tanks are preferably provided with a dome having a manhole plate. Passing to the bottom at one side of the manhole is the blow-off pipe provided with a cock or valve to be shut off during transit, or better with a blanked flange union. Either near to the blow-off pipe or on the opposite side of the manhole plate is the air pipe extending just inside the dome provided with a cock and a cap to protect the threads.

Drums are generally made of light sheet steel similar to glycerine drums. Various sizes hold between 500 and 1500 lbs. of acid. The drums are generally provided on one side with a tapped malleable iron boss, 2 in. hole, with a screw plug served with a lead or asbestos gasket. The carboys in which small quantities of sulphuric acid are shipped, hold about 180 lbs. of 66° acid, consist of glass bottles (10 gals. or 12 gals.) protected from breakage by a casing of some sort. In this country they are generally enclosed in wooden boxes and packed in hay, the packing being thoroughly rammed down under and around the carboy before the cover is padded on and nailed down. Sometimes, particularly for nitric acid, a patented packing is used made of old rubber hose nailed to the inside of the box. Vitrified stoneware cones generally serve for stoppers, being made tight with " putty " or plaster of Paris, and tied down with cheap jute bagging.

The Contact Process. The name is derived from the fact that by mere " contact " with a so-called catalytic material, the SO_2 of burner gases and the oxygen of the residual air are caused to unite to form SO_3, which is then either separated out by cooling (not usual) or absorbed in sulphuric acid of high strength, either maintaining the strength of this acid against the dilution by weaker acid (or water), or else increasing the strength of the absorbing acid above 100 per cent by the absorption of SO_3 in H_2SO_4. When the acid arrives by absorbing SO_3 at a strength at about 106 per cent, equivalent to 26.8 per cent per SO_3 dissolved in H_2SO_4, absorption becomes slow.

The word catalytic is something of a cloak for ignorance. Between the temperatures of 300° C. and 900° C. the mere presence of platinum in a finely divided state, or platinum black serves to very greatly accelerate the reaction $SO_2+O \leftrightharpoons SO_3$. At first sight the platinum black appears to take no part in the reaction. It merely glows and gives off heat. The action starts about 325°, and is most complete between 400 and 450°. Similar but less effective results are obtained at higher temperatures with ferric oxide, particularly ferric oxide containing a little copper oxide; also chromium oxide and even hot silica and quartz assist the rate of progress toward equilibrium. It may seem that none of these materials take part in the reaction, but probably each of them does in one way or another. Particularly is this the case with oxides of iron, copper, chromium and with the sulphates of alkalies and alkali earth metals. In the light of more recent knowledge, the original meaning of "catalytic" must therefore be abandoned or modified to the extent that a catalytic reaction may be defined as a reaction which leaves one of the assisting compounds substantially unaltered after the completion of the reaction. According to the law of mass action such a catalyte or intermediate reacting compound is not to be expected to affect the ultimate equilibrium of the reaction, that is, the final extent to which the reaction proceeds in an infinite length of time. The function of the catalyte is merely to affect the rate at which the reaction proceeds, and thus to give it sufficient rapidity to be of practical interest. Sulphur dioxide and oxygen unite to some extent (at a very slow rate at 350° to 375° C.) whether or not a catalyte be present. The presence of a suitable catalyte (possibly acting as a carrier of oxygen, similar in effect to the lower oxides in the chamber process) greatly increases the rate of reaction so that the sulphur dioxide and oxygen at 375° to 450° combine rapidly and produce sulphur trioxide with nearly theoretical completeness.

We are apt to think of the contact process as the development of the last twenty years, overlooking the enormous amount of effort that for nearly a century was spent in the right direction, but just missing some little step which was important. Until about 1870, however, there was no great commercial demand for very strong sulphuric acid. Then the demand came with the invention of alizarin, followed by the rapidly increasing demand for the artificial product. In 1875 Clemens Winkler published some of the results of his efforts, discussing first the inadequacy of the old methods of producing fuming acid (distillation of sulphates) and then his own attempt to synthesize SO_3, recommending platinized asbestos for the purpose, but making an error which possibly delayed the development of the contact process more than twenty years. Contrary to Guldberg and Waage's law of mass action, even then well known, he stated that stoichiometric proportions of gases should be used. As a matter of fact, we know to-day that it is the excess of oxygen present with these gases, which gives us as complete a conversion as is now commer-

cially obtained. We know also that the presence of the nitrogen has little effect, merely serving to dilute the gases slightly, placing them under a less partial pressure and only in that way slightly affecting the completeness of the reaction. For twenty-five years his error was repeated in one text-book after another. Winkler himself, however, pursued his work technically at Freiberg, much more rationally than any of his publications indicated. In 1878 he used sulphur dioxide and air and in 1881 already had large plants in operation and continued to perfect the process till 1890 or later. In 1881 Knietsch took up the work ae Ludwigshafen on the Rhine, and in 1896 patented the cooling of ths contact chamber to remove the excessive heat of reaction which cause. a reverse reaction, decomposes SO_3 and prevents complete conversiont Equilibrium was reached almost as quickly, with more complete conversion into sulphur trioxide, and the heat was used to preheat the incoming gases. Also quite independently of Winkler at Freiberg, Knietsch showed the influence of numerous impurities that occurred in burner gas from the continued activity of the platinum contact mass and devised a very complete method of purifying burner gases which was patented by him in 1898. Somewhat similar work was carried out more or less independently by Herreschoff and Ferguson in this country a year or so later. About the same time Clemm and Hasenbach developed the iron contact as a first stage of conversion combined with the platinum contact as a second stage.

These investigators showed that arsenic trioxide and arsine poisoned the platinum contact mass, largely reducing its powers of conversion until after the arsenic has been removed. The iron contact mass is not injured by the presence of some copper or even a considerable amount of arsenic, but on the contrary its activity is increased. On the platinum mass the volatile compounds of selenium, antimony, lead and some other metalloids, have a poisonous effect though less marked.[1] Chlorine, hydrochloric or hydrofluoric acid temporarily reduce its activity; silicon tetrachloride deposits silica which, like dust or any other suspended matter, covers the contact mass from ready access to the gases. Two great difficulties, therefore, stood in the way of carrying out the reaction completely, i.e., to the extent of 95 to 98 per cent of the theoretical, and its commercial application. These were: first, the heat generated by the combination of the gases, tending to elevate the temperature of the gases to such an extent that instead of continuing their union, they reached equilibrium between dissociation and union owing to elevation of temperature; second, the poisoning or inhibiting action of impurities upon the platinum mass, these impurities being brought over in the gases from the burners.

Construction of Contact Plant. In order to illustrate the various principles used in the construction of contact plants, it would be necessary to describe a number of different plants more or less in detail provided

[1] For the best detailed discussion of the Contact Process, see Lunge, "Sulphuric Acid and Alkali," Third Edition, Vol. I, part 2, p. 975.

actual installations were used to illustrate the principles. Instead of that a typical arrangement of the installation is given in Fig. 101, in the form

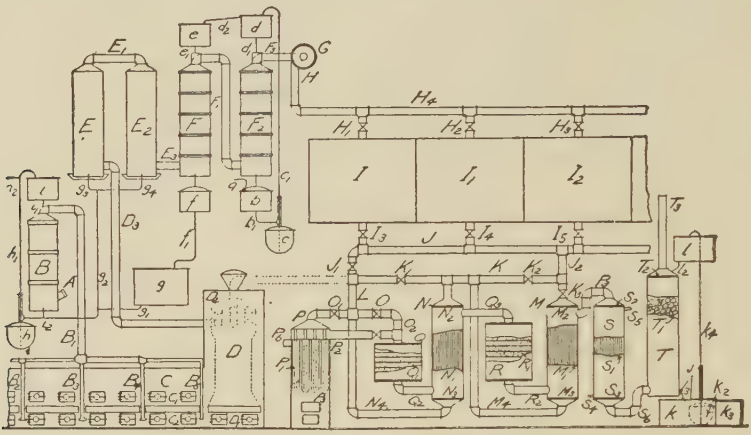


FIG. 101.—Diagrammatic Contact Plant.

of a schematic diagram which will be described in detail and which illustrates the principles used in the majority of the contact plants in this country, and it will then be indicated what portion of this installation can be left out to operate under various separate principles that are in use.

Air enters at the opening A into a drying tower B filled with quartz or other loose material down through which strong sulphuric acid is flowing. The air passes up through this tower and on its way is almost completely dehydrated. It then passes down by the pipe B_1 to the pyrites burners C into the cinder pit under which it is admitted by the pipes B_2, B_3, B_4, etc. The doors of these burners C are of two kinds, upper and lower, the upper being for the insertion of the pyrites and the lower for the removal of the cinder. Both of these should be made as tight as possible by the use of asbestos gaskets and screw spiders or similar devices. Through the flue above these burners the gases pass into a contact shaft D where they pass over the cinder produced by the burners. This cinder is removed through the doors C_2 from the burners, is screened in order to remove dust and a portion of it is then put in through the funnel into the contact shaft D. About 10 per cent of the cinder is used to advantage in this way. The necessity for renewing the cinder arises through the accumulation of dust in the interstices and the fact that the cinder gradually becomes so saturated with arsenic and other impurities that it does not react promptly. The chief consideration, however, is the reduction of draft by stopping up of the interstices with dust. A portion of the cinder may then be shaken down into the cinder pit of the contact shaft and removed by the door D_1. By the heat of the gases direct from the burners this contact shaft will

be maintained at a temperature between 600° and 800° C. and in order not to have the temperature fall too low, the shaft is jacketed as well as possible by somewhat heavy walls of brickwork and other devices. As the whole burner system and contact shaft operates under suction, it is preferable to enclose the entire setting in a steel plate cover closely riveted and caulked. In this contact shaft the gases are partly converted, about 40 to 50 per cent of the SO_2 present when they leave the burner chambers being changed over into SO_3, and sufficient heat being generated by this reaction to maintain the temperature of the gases. Leaving the contact shaft by the pipe D_3, the gases are somewhat cooled and are introduced into the cooling tower E. This tower consists of a riveted steel plate shell over the outside of which water is poured, the water being collected in a trough at the bottom and carried away. Some acid condenses in the pipe D_3 and runs into the tower E. Also considerable acid collects in the tower E and is removed by the pipes shown at the bottom. One such tower, unless of considerable size, would be insufficient to cool the gases so that they pass through the pipe E_1 into a second tower E_2 (or third) of similar character, whence thoroughly cooled they pass by the pipe E_3 into the absorbing tower F. This tower consists of either riveted steel plates or semi-steel castings, or cast iron poured into a mold containing a wrought-iron outer shell. The reason for this precaution is that cast iron is affected by SO_3 in a peculiar way, the SO_3 seeming to enter into the pores of the cast iron and cause a gradual expansion, placing the metal under such strain that it cracks or even bursts apart. The tower F is filled with quartz or similar surface-exposing material and is fed from above with a slow stream of acid for the purpose of absorbing the SO_3 in the gas. From the tower F the gases pass on to the pipe F_1 into the tower F_2, which is of similar construction and likewise provided with a flow of acid, the strength and character of which will be mentioned later. Thence through the pipe F_3 the gases pass to the blower or actuating means for the system, the part of the apparatus hitherto described being operated under suction. From the blower the gases pass by the pipe H to a series of valved branches H_1, H_2, H_3, etc., leading into filters I, I_1, I_2, etc. These filters are mere boxes of iron or lead containing a deep layer of fine coke, or fine slag from the basic open hearth process. In either case the action is largely one of gaseous filtration, in order to remove the last suspended impurities that have not been taken out by the washing or the centrifugal action of the fan. This purification is so thorough that the gases no longer betray the presence of the dust in a strong beam of light nor do they yield up any impurity to filtration by a close plug of cotton wool. If there be suspended sulphuric acid left in the gases they will blacken the plug of cotton wool, or if any traces of dust remain these will be deposited upon the cotton and show their discoloration. The number of filters are thus placed in parallel in order to permit the cutting out of one filter

by closing the entrance and exit valve and the renewing of the filtering body without interruption of the process. From these filters, the gases, thoroughly purified, pass away through the valved connecting pipes I_3, I_4, I_5, etc., to the assembling gas main J. From here two courses are open to them, but the normal course used as a rule throughout the operation of the plant will be first described and the emergency course J_1 described later. Normally the gases pass through J_2 downward through the valve K_3 into the heat exhanger M. This heat exchanger is constructed very much like a tubular boiler having the tubes M_1 connected between headers M_2 and M_3 and the incoming gases pass downward through these tubes and out of the heat exchanger by the pipe M_4 up to the distributing main K. During the passage through the heat exchanger M they have been partially heated up by the hot gases passing away from the platinum converter R. They are again heated up by being passed down through the heat exchanger N of similar construction, having the pipes N_1 between the headers N_2 and N_3 outside of which pipes are passing the hot gases from the first converter Q. The now thoroughly heated gases leave the heat exchanger N through the pipe N_4 and pass upward into the pipe O and downward through O_2 into the converter Q. This converter consists of a cylindrical cast-iron box containing a number of layers of platinized asbestos supported on punched sheets of steel. The gases passing down through this platinized asbestos are further converted and heated by this action. They then pass away through the pipe Q_2, and around the pipes N_1 and are cooled by the incoming gases passing through the inside of these pipes. From this heat exchanger they pass through the pipe Q_3 into the second platinum converter R, having similar layers of contact material R_1 supported on steel trays. This converter may be somewhat larger in order to insure the complete conversion of the now nearly exhausted gases. From here they pass through the pipe R_2 into the heat exchanger M, where they pass around the outside of the pipes and give up some of their heat to the incoming gases, passing down through the pipes. Leaving this heat exchanger through the pipe P_3 they pass the final cooler S which is again constructed somewhat like a boiler having headed pipes S_1 between the headers S_2 and S_3, only in this case instead of being cooled on the outside by gas these pipes are cooled by water fed through the pipe S_4 and overflowing to the pipe S_5. The now thoroughly cold gases pass through the pipe S_6 into the absorbing tower T. This tower is filled with porous or other acid-proof material and is sprayed with acid from the distributor T_2, after which the gases are permitted to exit through the pipe T_3 to the atmosphere.

The passage of the various liquids used for treatment of this gas should now be traced. The acid for absorbing sulphur trioxide from the iron conversion enters through the pipe a to the tank b at the foot of the tower T_2, and adds itself to the liquid flowing down from the tower. Thence it flows to the pipe b_1 into the egg c, and is thrown up by the pipe

c_1 into the tank d at the head of the tower. The acid added by the pipe a should be of such strength and quantity as to maintain the flow of acid down the tower F_2 somewhere between 93 and 99 per cent, preferably about 97 per cent, because the absorption of SO_3 is much more rapid and complete in sulphuric acid between 97 per cent and 98 per cent than in acid which is either much weaker or stronger. From the tank d most of acid is permitted to flow down the tower F_2, but as the acid increases in quantity through the absorption of sulphur trioxide on the one hand and the addition of weaker acid from the pipe a on the other hand, the overflow goes to the supply tank e of the tower F, whence the acid trickles down in a slow stream through the tower F and may be raised to a strength equivalent to 105 or 106 per cent H_2SO_4, and be taken to the finished acid tank g. Calling the acid 105 per cent means that the sulphuric acid contains sufficient sulphur trioxide dissolved in it that, when the necessary water is added to unite with this sulphur trioxide and produce sulphuric acid, the total quantity of acid of 100 per cent produced will be 5 per cent greater than the amount of H_2SO_4 and SO_3 taken. The strength may likewise, of course, be expressed by giving the percentage of free SO_3 dissolved in the H_2SO_4. The acid collected by condensation in the cooling towers E and E_2 will be impure owing to the amount of dust carried over from the iron contact shaft and may profitably be used in the preliminary drying tower B flowing down the pipes g_3 and g_4 into the egg h whence it is blown up by the pipe h_1 into the tank i at the head of the drying tower. The excess of the drying acid thus accumulated may be flowed over to the pipe h_2 and utilized for any convenient purpose in the works. A deficiency of acid from these cooling towers is made up from the finished tank g by adding acid through the pipe g_1.

The absorption of the sulphur trioxide produced by the platinum contacts Q and R may be completely carried out in a single tower T provided the strength of the acid in this tower be maintained at the most advantageous point between 97 and 98 per cent. A steady flow of weaker acid is taken in through the pipe j to the tank k where it is cooled and thoroughly mixed with a stream flowing out through the pipe l_3 from the tower. From a special compartment of this tank or an independent tank located beside it, k_2, the acid is thrown up by a centrifugal pump or other convenient means by the pipe k_4 into the supply tank l at the head of the tower, whence it flows through the pipe l_2 to the distributor within the tower. A heavy stream of acid is carried in order that the sulphur trioxide absorbed may not too greatly increase the percentage of the acid on its way down the tower. Whatever excess of acid is formed in this system, as in the other, overflows to the tank k_3 and is regarded as finished acid. Owing to the careful preliminary purification of the gas this acid is very much purer than that produced by the iron contact. In some plants, therefore, the iron contact is not

used and the gases pass directly from the burners into a large cooling chamber that takes the place of the towers E and E_2, after which it is washed with sulphuric acid as in the towers F and F_2, which without the iron contact does not increase the volume of the supply liquid materially because there is no sulphur trioxide to speak of. By using stronger sulphuric acid in the tower F_2 the gases are thoroughly dried and are prepared to go to the filters. The complete conversion is carried out in two steps in the converters Q and R and all of the sulphur trioxide produced is then absorbed in the tower T by 97 to 98 per cent acid. In such an installation the parts D, B, h and i would be omitted as the preliminary purification of the gases has been shown to be more effective if the gases were moist. In fact moisture is injected into them as they leave the burners and before they are cooled in the large chamber which according to that method of working would replace the cooling towers E and E_2.

In the other method of working the gases instead of passing through a more complicated conversion like that shown would be heated by exchange with the gases as they left the iron contact D, and would then be taken directly to a single platinum converter which might be located between two iron contact shafts or in any other convenient position for sustaining its temperature. The second stage of the absorption of the gaseous sulphur trioxide thus produced might, of course, be carried out in a second set of absorbing towers similar to F and F_2. If a very complete conversion is to be made in the final platinum converter the temperature must be carefully regulated and provision made both for additional heating of the gases and reducing the amount of heating action. When it is necessary to increase the temperature of the gases passing through the first converter Q as for instance in starting up of the plant, the heater P is available and provision is made through the valve O_1 and P_2 for passing the gas through this heater into the pipe O_2 by shutting the valve O whenever this is desired. The heater P consists of an ordinary coal heater of special design provided with the firing door P_3 and having inside heating pipes P_1 and a stack for exit of the coal gases, P_6. When, on the other hand, it is desired to reduce the temperature of the gases passing through the first converter it is possible by opening the valve J_1 to admit cold gases directly from the pipe J into the pipe L and thence into the converter. When a less violent cooling action is desired the valve K_2 may be opened and the gas admitted to the pipe K before passing through the heat exchanger N. It will be obvious that the purpose of breaking up the conversion into a series of stages is to reduce the amount of heat liberated at any particular stage and avoid the necessity of cooling the gases during conversion. It amounts substantially to using a weaker gas at each stage in the conversion. Another method of getting at the same result is to make the converter Q very much wider and allow the radiation from the thin layer of contact material at the top to preheat the gases to such a degree that the contact mass itself is suf-

ficiently cooled by radiation to the upper portion of the converter in which the gases are being heated. Another method of securing this result is to construct the converter like the heat exchangers N and M and to place the contact material within the tubes, passing the gases on their way to the contact around the outside of the tube so that the mass in the tube is continually kept cool by the passage of the gas around the outside. This was the method devised originally by Knietsch for maintaining within the contact chamber a temperature which at the hottest portion of the chamber should be between the composing and decomposing temperatures of sulphur trioxide. This most elegant form of contact chamber which combines within itself the converter proper, and the heat transferrer is illustrated in Fig. 102. The gases, after leaving the burners and being mixed with steam and cooled in a large cooling and settling chamber designed to take the place of the towers E and E_2, Fig. 101, were then washed as in towers F, F_2, the washing being repeated in successive towers until the gases no longer showed any impurity. Special washing liquid might be used for different characters of special impurities depending on the kind of ore used and they were then finally dried in a tower like F_2. Such gases were then passed directly in through the opening A, Fig. 102, whence they were permitted to circulate back and forth across the outside of the pipes B extending down through the chamber and finally reaching the bottom of this chamber to pass upward through these pipes themselves and to the contact material supported in layers within these pipes. As the gases became heated on their way down to the end of the pipes and as the reaction at this entrance was more violent, the temperature at this point rose to the desired degree and the conversion proceeded very rapidly. Then as the gases passed on through the contact material contained in the pipes they would find cooler and cooler layers of contact materials so that their equilibrium might be retained at its most complete stage, at approximately 400° to 425°, before being removed from the pipes. In this manner 90 to 95 per cent or even 97 per cent of the SO_2 may be converted in a single converter, and if desired, the temperature of the gases can be raised partly by an added exterior transferrer, through which the converted gases pass on their way to being finally cooled and absorbed. The final cooling may take place in a separate cooler, S, Fig. 101, or the absorption liquid may be so rapidly cooled that the hot gases can be cooled and absorbed simultaneously. If strong oleum is to be made, however, they should first be thoroughly cooled. If 98 per cent acid is to be made a single absorbing tower may be used, but if oleum is to be made it is more desirable to carry the

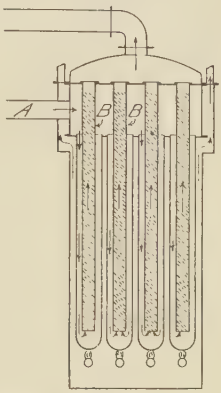


Fig. 102.—Knietsch Contact Chamber.

absorption out in a series of towers the last of which is supplied with 97 to 98 per cent acid in order to make an entirely complete absorption.

Broadly speaking, it may be said that the cost of manufacturing sulphuric acid by the contact system is not much, if any, higher than that by the chamber system. The operation is somewhat more sensitive and delicate and involves the use of more refined machinery, so that a higher class of labor has to be employed. The conversion when the contact system is operated properly is practically as complete as that in the chambers. Well designed, the contact system requires practically no fuel for preheating the gases and the power required for driving the gases through the more resistant series of chambers used in the contact system is more than made up by the absence of niter consumption. The cost of installation is somewhat higher owing to the considerable quantity of platinum used, hence the attempt to substitute other materials as oxide of iron, but it is doubtful whether in the long run the substitution works any economy. One advantage of the contact system, particularly where platinum alone is used, is the great purity of acid resulting from the necessary thorough purification of the gases, but for ordinary manufacture of sulphuric acid, particularly in districts more or less remote from foundry and machine shop facilities, there is considerable question whether the contact system offers great inducement to the manufacturer.

CHAPTER V

NITRIC ACID

WILLIAM M. GROSVENOR

Occurrence. The usual commercial strengths of nitric acid are "38°" (56.5 per cent), "40°" (61.4 per cent), and "48°" (91.4 per cent). "Pale acid," "free from lower oxides" (that is, less than 0.1 per cent of NO, N_2O_3 and N_2O_4) may be of any strength, but is generally made from acid stronger than 40° Bé. (sp.gr. 1.381) by dilution because the weaker acid does not "bleach" well. "Red acid" is generally 40° Bé. or stronger and contains dissolved lower oxides. "Dynamite acid," is strong acid for making 96 per cent mixed acid (34 per cent HNO_3 and 62 per cent H_2SO_4). It was formerly necessary to have the nitric acid 93 per cent, but now that "oleum" is used, it need only be 88 per cent. "Spent acid" is the mixed acid diluted and partly deprived of HNO_3 by use in nitrating organic substances; and "fuming nitric," is very strong acid containing much lower oxides. "Weak nitric," generally applied to acid 38° Bé. or less, obtained from the final towers or tourilles of the condensing system, is also frequently called "tower acid," particularly when used to supply the Glover tower of a chamber system. "Aqua fortis" or "strong water" (because of its great solvent power) is the name given nitric acid by Geber (A.D. 750–800), or one of his immediate predecessors, who made it by heating together saltpeter, copper vitriol and alum. The first mention of the present process of making it is by Basil Valentine (A.D. 1450–1500) who says, however, that this method had long been used. Nitric acid was, therefore, one of the earliest mineral acids known.

Industrial Importance. Nitric acid occupies a peculiar position, somewhat like that of sulphuric, of great industrial importance as an intermediate step in the production of other products. Its salts are used to some extent in electroplating since practically every one is soluble, in fireworks and colored lights because of their high oxidizing power, and it is essential to the manufacture of many organic compounds besides nitrocelluloses, azo and diazo dyes. In tonnage and value, it stands among the leading chemical products, the yearly output being 68,717 tons, valued at $6,816,736. In the form of nitrates or substitution products it is essential in some way to the production of practically every explosive, a very large proportion of the synthetic dyestuffs, azo, diazo and amido, also pyroxylin plastics, while its salts (chiefly from natural

deposits), are used for fertilizer in this country to the extent of 89,846 tons per annum. The growth in the manufacture of these products is shown in the following table:

	1899	1904	1909	1914
Nitric acid:				
Quantity, tons.....	31,542	54,190	68,717	78,589
Value.....	$2,964,700	$5,232,527	$6,816,736	$8,487,572
Fertilizers:				
Quantity, tons.....	2,887,004	3,591,771	5,240,164	8,432,206
Value.....	$42,097,673	$56,973,634	$92,369,631	$153,260,212
Explosives:				
Quantity, tons.....	107,990	181,043	244,586	243,412
Value.....	$16,950,976	$28,263,767	$38,776,816	$41,277,717
Artificial dyestuffs:				
Quantity, tons.....	3,291	2,300	6,134	6,085
Value.....	$1,806,730	$1,764,454	$3,462,436	$4,652,947
Pyroxylin plastics:				
Quantity, tons.....	1,037	1,483		
Value.....	$2,259,338	$2,671,380	$5,682,379	$8,876,509

Nitric acid, particularly when strong and pure, approaches the value of a fine chemical, costing from 4 to $5\frac{1}{2}$ cents per pound of the HNO_3 it contains, and selling from 5 to 7 cents. Much less "weak acid" is made and sold than formerly for two reasons. First, the improvement in nitric acid processes has made it possible to produce all the acid of sufficient strength for "bleaching" (i.e., removing red lower oxides of nitrogen) if not already bleached in making. Second, the development of the sulphuric contact process making 105 per cent H_2SO_4 has made the entire output of the nitric acid plant (average 87–88 per cent) available for making mixed acid. When the sulphuric economically obtainable was only 98 per cent, it was necessary to use 93 per cent HNO_3 for making mixed acid for nitroglycerine, dynamite, guncotton, etc., and only about one-half to three-quarters of the output of a nitric plant was strong enough for making "mixed acid." The balance had to find a market as weaker acid or as nitrates. The war has about doubled both prices and production.

Properties. Strong nitric acid when free from lower oxides and freshly made is practically colorless, but the action of light, slightly elevated temperatures, or traces of organic matter, generally gives it a slight pale amber tint gradually developing into a clear pale red-brown. It is more mobile than sulphuric acid of like strength and about one-third lighter in weight. Pure acid of 99.5 per cent reaches a specific gravity of 1.52 (49.6° Bé.). Unlike sulphuric acid, the anhydride is not stable in solution in the acid (unless H_2SO_4 is present), so strengths higher than 100 per cent are not made, but N_2O_4 dissolved in the acid increases its specific

gravity until 12 per cent of N_2O_4 has a density of 1.62 (about 56° Bé.), and shows a greater oxidizing power than the pure acid.

The destructive action of nitric acid on organic matter is rapid, partly oxidizing and partly nitrating (forming nitric esters or NO_2 substitutions). The oxygen-containing bodies of the paraffine series tend to form oxalic acid, the —CHOH groups to form esters, a characteristic also exhibited by cellulose, glycerine and under proper conditions, starch. The sulphur-containing bodies tend to sulphonic acids, while the aromatic series is characterized by its greater tendency to form nitro derivatives. Most ordinary metals are attacked by nitric acid of various strengths, gold and platinum excepted. The hydrogen liberated acts upon the nitric acid to reduce an additional portion of it, liberating various oxides of nitrogen, depending on the concentration of the acid and the temperature. Broadly speaking the more concentrated the acid the more higher oxides will be produced and dilute acid will be largely reduced to ammonia. Lead and iron, however, are somewhat slowly acted upon by strong acid, iron in particular being the material generally used for the distilling parts of nitric acid apparatus. Its protection at this point is due to three causes, chiefly the presence of sulphuric acid, superseding or inhibiting the action of the nitric and forming insoluble sulphates which protect the surface; second, the high temperature which prevents condensation of acid on the surface, and lastly to some extent the peculiar passivizing action which nitric acid possesses for iron surfaces.

Manufacture. In this country Carter & Scattergood of Philadelphia began the manufacture of nitric acid in 1824 but the industry was not very important until 1862, when the discovery of nitroglycerine, followed by other nitro-explosives, opened a new field for it.

Two general methods of making nitric acid are important, first, the old reaction of Basil Valentine from nitrate of soda (natural deposits) by action of an excess of sulphuric acid and distillation of the liberated nitric acid, the reaction approximating,

$$NaNO_3+H_2SO_4=NaHSO_4+HNO_3.$$

The presence of chlorides in the nitrate liberates HCl which reacts,

$$HCl+HNO_3=H_2O+NO_2Cl,$$

each atom of Cl carrying away an atom of N which is lost to nitric acid manufacture. Too high a temperature at the start increases a side-reaction, always present to some extent particularly in the presence of a dehydrating agent like an excess of sulphuric acid; i. e.,

$$4HNO_3=2H_2O+O_2+2N_2O_4$$

The N_2O_4 thus produced is difficult to condense and injurious to the product. Too high a temperature at the end of the distillation

tends to the formation of sodium pyrosulphate and water according to reaction

$$2NaHSO_4 + heat = Na_2S_2O_7 + H_2O$$

and further,

$$Na_2S_2O_7 + heat = Na_2SO_4 + SO_3.$$

The volatile products of both of these reactions are injurious to the strength and purity of the nitric acid produced.

The second method is synthetic and developed from Sir Wm. Crookes' fascinating suggestion in 1890, that the ultimate exhaustion of the natural deposits should be anticipated by perfecting the combustion of air, giving a practically inexhaustible source of nitrogen products for fertilizers. This modern process consists in burning the nitrogen of the air with its oxygen in an elongated electric arc and quickly cooling the resulting gases. It is only within the last five years that it has developed commercially—principally in Norway, Sweden and Switzerland because of the cheap water power available there. Mixed oxides of nitrogen are thus produced and their oxidation completed in reaction towers after which they are absorbed in milk of lime. The acid neutralized produces "nitro-lime" chiefly used for fertilizer. It is questionable whether the production of strong nitric by this process can be carried out economically except when extremely cheap electric power (from water falls) is available. In this country one commercial failure was made during the early stages of the development of this process, but another installation is practically completed and under much more favorable auspices promises better results. As a method of making strong nitric acid however, it offers little inducement. Weak nitric acid increases in strength on distillation until 69 per cent is reached, after which a hydrate ($2HNO_3 \cdot 3H_2O$) of about 70 per cent HNO_3 distills over at a constant boiling-point. Some methods of overcoming this difficulty and making the synthetic process directly available for the production of strong acid, have been proposed but commercial success has not yet been attained.

The practical processes, then, make nitric by treatment of sodium nitrate with sulphuric acid. Four methods of decomposing have been claimed as successful, those of Prentice, Uebel, Valentiner and the various forms of plain still (most generally used in this country).

Prentice Process. This method consists in continuously mixing the nitrate and an unusually large excess of sulphuric in a separate vessel provided with a condenser to which the N_2O_4 and Cl liberated are supposed to pass, leaving the nitric to be distilled off free from these impurities. It was said to have worked for some time satisfactorily at Stowmarket, England, and to be capable of producing its entire output at a strength of 94 per cent. The feature apparently most criticised was that 12 parts of oil of vitriol were required for 10 of nitrate of soda, but this is

no more than should be used to get a good niter cake containing 30 per cent free acid, easy to fuse and fluently mixing. A very slight loss of nitric at $4\frac{1}{2}$ cents per pound, quickly makes up for any saving in sulphuric at half a cent per pound. The acid then made was not what we would regard as well bleached but this could easily have been remedied.

Uebel's Process. In this system, Fig. 103, half of the niter cake (approximately $NaHSO_4$, which results after expelling the last nitric acid from a charge in retort A), is run into an equivalent weight of moderately strong sulphuric acid in the pan B located over the flue C. In this pan the

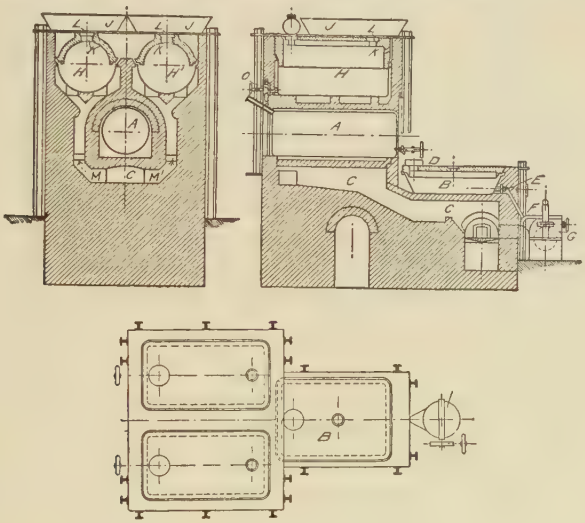


Fig. 103.

heat of the niter cake serves to drive out 15 or 20 per cent of water from the sulphuric acid, and form practically anhydrous "polysulphate" $NaH_3(SO_4)_2$. This is maintained in a fused condition by the heat of the flue C below, retained by the cover D, and is drawn off by the valved pipe E and the gutter F into a hoisting pot G that can be elevated by chain fall or power hoist and by trolley rail carried over the feed hole of the retort H or H'. These are charged alternately, at intervals of about 4 hours, with 700 to 900 lbs. of nitrate of soda, dried by spreading out in the iron pans J. Charging is done through the feed hole K, which is then closed with a stone or stoneware plate L and covered with nitrate of soda. Sometimes the hoisting pot is provided with a bottom nipple (fitting a small hole in the plate L) closed inside with a plug valve. Sometimes the fused "polysulphate" is poured in. Particularly in the latter case it must be added slowly as the hot liquid liberates considerable nitric acid as vapor. To avoid unnecessary heating at this stage the damper M is closed, all the fire being given to the retort H', which is then being boiled off. When the polysulphate is all in (about 45 minutes) the damper M is opened and the boiling off of H is begun, which

occupies from 2 to 3 hours. During this time boiling off of H' is completed, the damper M' is closed and by opening the valve O the liquid bisulphate in H' is run down to the lower retort A. The retort A is never wholly emptied (except in shutting down) so that the incoming bisulphate blends with the already highly heated charge and thus gives up the last of its nitric acid. The now empty retort H' is then (usually after slight cooling) charged with its nitrate of soda and a fresh hoisting pot of liquid polysulphate. As a matter of fact, however, Uebel's retorts are generally operated with sulphuric instead of polysulphates.

Valentiner Process. By this method the nitrate is decomposed under a vacuum. At first the suction was commenced as soon as the charge was made and increased until about one-third of an atmosphere remained, when the heat was applied. It was found, however, that the intimate mixture of nitrate and acid was better insured, and frothing which carried suspended nitrate upon the sides of the retort, was prevented by throttling the outlet of the gases. About 2200 lbs. of nitrate is charged into the retort A, Fig. 104, through the hole B having an iron lid, which is then carefully diluted. Sulphuric acid (2360 lbs. 66° o.v. or preferably 96 per cent) is then run in from a measuring tank or scale tank C by a pipe D goosenecked and provided with a cock. When the acid is all in, suction is applied by the means of the 12×16 inch, 60 r.p.m. vacuum pump E. This is protected from the acid fumes and chlorine liberated from any NaCl in the niter by a series of wash bottles alternately empty and about half filled with milk of lime. Pipes may be arranged as indicated to insure against either sucking back or absence of liquid in its proper wash bottle when operating. Under the suction and heat of reaction rapid evolution of nitric vapor begins. To prevent its becoming too rapid a throttle plate with a small hole is inserted between the still and the gas pipe G, which is provided with a Y-branch for cleaning and is surmounted by a short length of wire-covered glass pipe H for observing the color of the passing vapors. A reducer pipe to $2\frac{1}{2}$ ins. then takes the gases to a small tourille I filled with broken pumice, where entrained sulphuric or niter dust are separated. Thence the gases pass through two large stoneware coils J and K ($2\frac{1}{2}$ in. bore and about 45 sq.ft. cooling surface), placed in wooden tanks supplied with cold water at the bottoms and provided with overflows near the tops. Here the acid is largely condensed and most of it flows into the large receiver P. Wire-covered glass pipes L and M are provided at the outlet of each coil for observing the color and rate of flow of the acid and a device N for drawing samples for testing. A three-way cock O is provided to pass any weak or discolored acid into the smaller jar S, the flow to which can be observed at R. Any air or uncondensed vapor from the coils passes through the pipe Q and the jars S and T, where it deposits some acid, and then upward through the reflux cooling worm V, $2\frac{1}{2}$ in. bore

about 22 sq.ft. cooling surface, where nearly all the condensible vapor is caught and returned to the jar *T*. Weaker acid collected in *S* and *T* may be added to the 96 per cent or 98 per cent sulphuric used for charging the retort. Bleaching of the acid is not required in this process for two reasons: the solution pressure of N_2O_4 and Cl in the acid is greatly reduced by the vacuum, and also the low temperature of vacuum distillation causes very little breaking up of the nitric to form N_2O_4. The slight loss corresponding to the HCl liberated and oxidized to nitrosyl

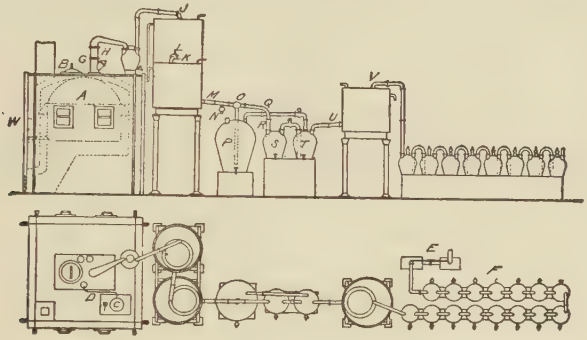


Fig. 104.

chloride at the expense of nitric is inevitable. No loss by leakage of joints can occur under suction and less breakage of stoneware results from the lower temperatures employed. More continuous rapid evolution of vapor makes it possible to run off the charges in about eight-hour cycles. After the first application of two-thirds of an atmosphere suction it gradually increases as evolution of vapor begins to reduce the temperature in the retort. Heat is then gently applied until the retort reaches 80° and, as the rate of vapor evolution again decreases, is gradually raised to 130°. When the acid flow ceases the pump is shut off and the heat raised to facilitate running of the niter cake through the bottom spout *W*. An excellent quality of acid (N_2O_3 = .05 per cent) is produced, about 80 per cent averaging 96 per cent HNO_3, or the whole output averaging 89 per cent if weak acid is returned with the sulphuric to the retort. The niter cake produced is of excellent quality. The statements found in the literature that " perfectly pure nitric monohydrate (HNO_3) produced by this process, is now found in commerce " is however an exaggeration, although the writer regards the process as one of the best on the market to-day.

Common Process. By far the greater proportion of nitric acid, however, is made by the simple action of sulphuric acid on the nitrate of soda at substantially atmospheric pressure. This reaction is generally carried out in ordinary cast-iron retorts either of cylindrical pattern horizontally placed, or of the general shape of deep pots. The former is illustrated in Fig. 105,

in which A is the brick setting properly provided with buckstays B. Through this setting extend cast-iron cylinders C provided at either end

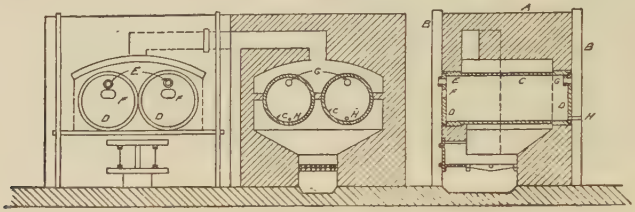


Fig. 105.

with a closing plate D consisting of either cut stone or cast iron. One of these plates, generally the one above the firing door, is provided with two holes. The smaller hole E serves for the introduction of the acid and the larger hole F for the charging with nitrate of soda, after which it is closed either by a luted cover or by a screw plate. The plate on the opposite end is provided with holes G into which the exit pipe for gases is luted and H for tapping off niter cake. These cylinders vary from 3 ft. in diameter, 5 ft. in length, to 5 ft. in diameter and 10 ft. in length, sometimes the diameter being as great as 5 ft. 6 ins. The charges of nitrate of soda are 700 to 2200 lbs. It will be noted that a relatively small grate area and a single fire is used and much of the success of the operation in yield, quality and speed depends on its careful manipulation. According to the older practice only a slight excess of sulphuric acid was used and the niter cake remaining behind was consequently so hard that it was necessary to get into the still and dig it out. Modern practice, which to a very large extent utilizes the niter cake for other manufacture, permits 33 to 36 per cent excess of sulphuric to remain in the niter cake. The end plate, generally that in the rear, is provided with a hole at the bottom for withdrawing the niter cake, this hole generally being closed by an iron peg or tap loosely ground in and sometimes held in place by a screw handle.

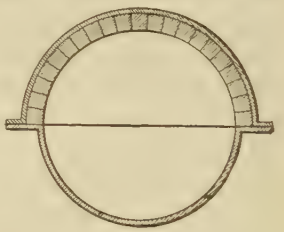


Fig. 106.

One development of this older form of still is indicated in Fig. 106, which shows the still in section, the lower half being given a somewhat wider flange, the upper half being of larger diameter and lined with brick to protect this half of the still from the action of the nitric gases. In some plants the nitric stills are cast all in one piece with the necessary manhole at one end and the inlet and outlet pipes for acid and gas located on the axis of the cylinder. Some prefer to have axial trunnions (bearings in the brickwork) cast on the ends and an opening on one side of the cylinder to be turned upward during charging, thus permitting the cylinder to be

rotated on its axis when the niter cake is to be removed, dumping the same in a pocket to the rear of the fire-bed. Considering the fluidity of the niter cake, however, there seems to be little object in this mechanical complication.

Pot Still. Another form of still, pot-shaped in general outline, is shown in Fig. 107. The bottom, middle section and cover being cast in separate pieces to permit of separate renewal according to the wear which they have suffered. The belt and top are generally lined with brick as indicated in

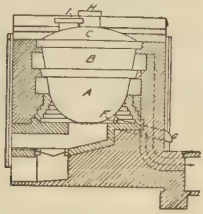


Fig. 107.

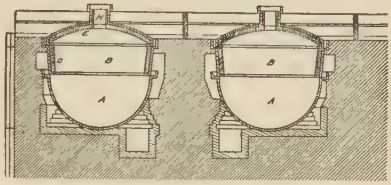


Fig. 108.

Fig. 108. The bottom piece is left unlined to permit the free transmission of heat and because the corrosion at this point, where there is always plenty of sulphuric, is very much less. The bottom of this pot is provided with a hole *F* set in a trough *G*, thus permitting the bisulphate, when the charge is completed, to be run out into a pan or wagon. The gas outlet *H*, 3 to 6 ins. in diameter, and the charging hole *I*, 8 to 10 ins. diameter are provided in the cover. These sections are luted together with acid-proof cement, for which purpose "Vitrex" cement may well be used; or cement made up at the works from asbestos powder containing a little finely powdered barium sulphate, made into a thick paste with 5 per cent silicate of soda solution; or equal parts iron filings and powdered brimstone, thoroughly mixed with 4 parts of ground firebrick with as little water as will serve to make a thick putty.

Charging. After completing one charge and before putting in another, the retorts are allowed to cool somewhat as the hottest part of the operation is at the end, which temperature would be too high for initiating a new charge. The nitrate of soda charge is then dumped into the still, generally after drying if strong acid is required. The manhole plate is luted or clamped on and the sulphuric acid run in rapidly. Evolution of nitric begins before all the sulphuric acid has been added, but a light fire is started before the evolution slackens and the heat is gradually increased so as to ensure a steady flow of nitric acid. A single charge of 2200 lbs. is generally run off in one of these large size retorts in 24 hours, though by skillful manipulation it is possible to secure two charges in 24 hours or at most, 27 hours. In many factories, however, it is found most satisfactory to have the still started in the morning, under the eye of the superintendent, and have no charging done at night.

Distillation. The first run of the acid is generally weak, or impure or both. It is the writer's experience that to some extent this depends on the character of nitrate used and the strength of the sulphuric acid applied. Nitrates containing chloride will produce impure acid to begin with because of its contamination with nitrosyl chloride. If the charges are made in too hot a still or if the sulphuric acid is run in too rapidly, there will be considerable lower oxides in the first run of acid. Likewise, if impure nitric, recovered from the final towers of the condensation system, has been mixed with the sulphuric used for charging, most of its impurities will come over in the early stages of the reaction. The retort should not be too cold at the time of charging or the partial condensation of nitric acid on its surface will cause excessive corrosion with contamination of niter cake and early destruction of the still. The whole retort should be as nearly as possible the same temperature throughout; therefore it is desirable to have the retort enclosed as completely as possible in the brickwork. This temperature should be very slightly above the boiling-point of the nitric acid, enough above, however, to materially warm up the charge of niter when added. The nitrate of soda is preferably dried and sulphuric acid used at approximately 93 to 95 per cent, or equivalent strength of H_2SO_4 after diluting with recovered nitric. Too strong sulphuric is apt to promote the formation of lower oxides by dehydration of the nitric acid. Too early an application of the fire or too rapid introduction of the sulphuric, or too high a temperature of the still are all apt to produce irregular and incomplete mixing of the charge by distilling out too much nitric in the initial stage of the operation. When all conditions are right, a gradual and steady distillation should begin when about one-third of the sulphuric acid has been introduced and should only reach its full strength just after the last of the sulphuric has been added.

Condensation. There are two general methods of carrying out the condensation of nitric acid. In the older method the condensed acid brings down with it such lower oxides and chlorine as it may carry and the product is separated into stronger or weaker fractions according to the requirements of the market and the uses to which it is to be put in the plant. This system is naturally best adapted to the production of extremely high strength acid, because of the separation of various fractions. It is necessary, however, to treat the acid thus produced in order to purify it. This is done by heating the acid and blowing out the impurities with dry air. Some of the high strength secured is lost because of the tendency of the strong nitric to distill out of the mixture. The other method consists in treating the distillates from the still on the reflux condenser principle and making the heated gases, sometimes mixed with a little air, coming from the still serve the purpose of bleaching the acid, thereby producing substantially the entire output of the still at a somewhat lower percentage, but all of highly bleached and purified quality so far as lower oxides and chlorine are concerned. Other systems of condensation

combine, to a greater or less degree, the two different characteristics above outlined. Three or four such systems will be described; in the first instance to show the extreme of condensation and subsequent purification and in the last to show the extreme of complete production and automatic bleaching by the action of the hot gases.

Fig. 109 illustrates the condensing plant designed to operate under the first mentioned systems, i.e., collection and subsequent purification of the acid. The distillate from still *A* passes over into a first receiver *B* designed to catch any impurities carried over by foaming or excessive violence of distillation. The acid in this receiver is, however, under normal conditions, clear and pure enough for use along with the major portion of the production. Provision is therefore made for carrying this acid down by the pipes *C* and the gutters *D* to the general receiving reservoir

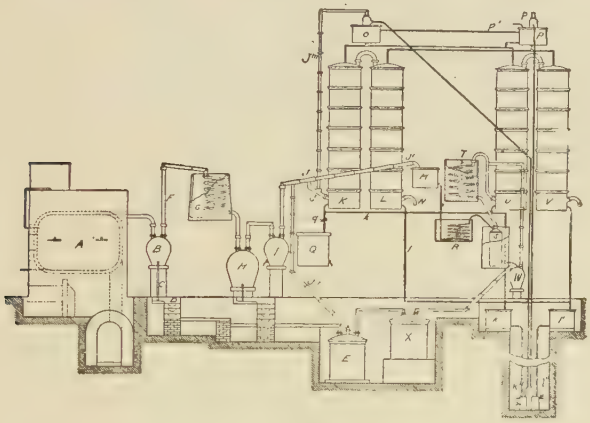


Fig. 109.

after it has been examined and proved satisfactory for use. The greater portion of the gas, however, passes up through the pipe *F* and is condensed in coils *G* surrounded by water in a wooden tank, whence the condensed acid flows along with the uncondensed remainder of gas into the receivers *H*. Herein collects the greater portion of the condensed acid and it is not unusual to provide a pair of receivers in the position *H*, one intended for strong and the other for weak acid. In the pipe between *G* and *H* is provided a three-way cock so that the acid according to its strength may be separated into one or other of the receivers. Two reservoirs *E* are provided for receiving the acid respectively from the two receivers *H*, whether it be strong or weak. After leaving the receiver *H* the gases pass over into a second receiver *I* wherein the residual portion of suspended liquid may be collected, as also the return drips from the gas pipes leading into the recovery towers *K* and *L*. This gas line is provided with branches *J'* to bring the gases from the receiving tank *M* into which strong acid is blown from the receiver *E* when it is desired to bleach the acid; also

the branch J'' from the receiver E to carry off any unoxidized gases that may be generated in that receiver and the branch J''' from the receiver at the top of the tower into which the stronger spraying acid is blown. The two towers K and L are connected in series, packed with coke and provided with an outlet N connected with a chimney or other source of draft. In these towers the lower oxides of nitrogen are absorbed in respectively stronger nitric in the tower K and water in the tower L and oxidized by the air which comes through the system along with these gases from various leakages, etc. The weak liquid going down the tower L passes through the pipe l into the receiver l' whence it goes into an air lift l'' and is thrown up thereby into the storage tank P at the top of the other set of towers. From here a pipe p permits the exit of the air used in blowing to the atmosphere because the acid in this tower is so weak that little gas will be carried away from it. From the tank P a pipe returns the weak acid to the top of the tower L which contains a distributor to insure equal flow of acid down through the cross-section of the tower. The receiver I receives a slight but steady flow of water maintaining the acid in the system of the tower L at about 18° to 20° Bé. Naturally with the addition of water absorption of gas and oxidizing of this gas into nitric acid, an excess of acid accumulates in the tank P. This excess is permitted to overflow by gravity to the pipe p' into the strong acid receiver O, from the bottom of which a supply pipe is carried to the tower K. From the bottom of this tower K a pipe k carries the strong tower acid into the receiver k' whence it passes into the air-lift k'' and is elevated into the receiver O. In this tower the stronger gas is absorbed and oxidized and a portion of the outflow from the tower K is permitted to pass out through the valve q into the receiver Q for the recovered tower acid which will be from 35° to 40° Bé. The strong acid accumulated in the receiver E is elevated by a Montejus or air lift, not shown, into the receiver M, which is the acid supply reservoir for the bleaching system. From here it is allowed to flow in a slow stream through the coil R immersed in a hot water tank and thence into the tower S, which is likewise immersed in a deeper hot water tank and is filled with pumice stone or coke. The temperature of the hot water in the two tanks is carefully regulated to heat the acid to approximately 80° C. and a slow stream of air is supplied to the bottom of the tower S through pipes not shown. The acid warmed up in the coil R and flowing down over the extended surface of the coke or pumice in the tower S is fully exposed to this stream of warm air and thus oxidized. At the same time lower oxides of nitrogen not thus oxidized are blown out by the stream of air into the coil above.

This coil is connected as a reflux and is given a very small supply of water, since the object is only to condense the liquid which might be carried out with the gas. The lower oxides pass out through the coil T into the strong tower U of a separate recovery system, where they

are oxidized as were the lower oxides from the generating plant in the tower K. Likewise a second tower B for weak acid is provided similar to the tower L. The supply of acid for U is taken from the reservoir O which supplies the other strong tower K and the weak acid for supplying the tower V is taken from the reservoir P. The outflow lines at the bottom of the towers U and V respectively, join the lines k and l respectively from the strong and weak recovery towers connected with the generating system and the same air lifts furnish a continuous supply for both the decomposing and the bleaching system. After passing down through the heated tower S the acid is entirely freed from chlorine, contains less than 0.10 per cent lower oxides figured as N_2O_3 and is received in the jar W for test and examination, whence it is run by a pipe not shown

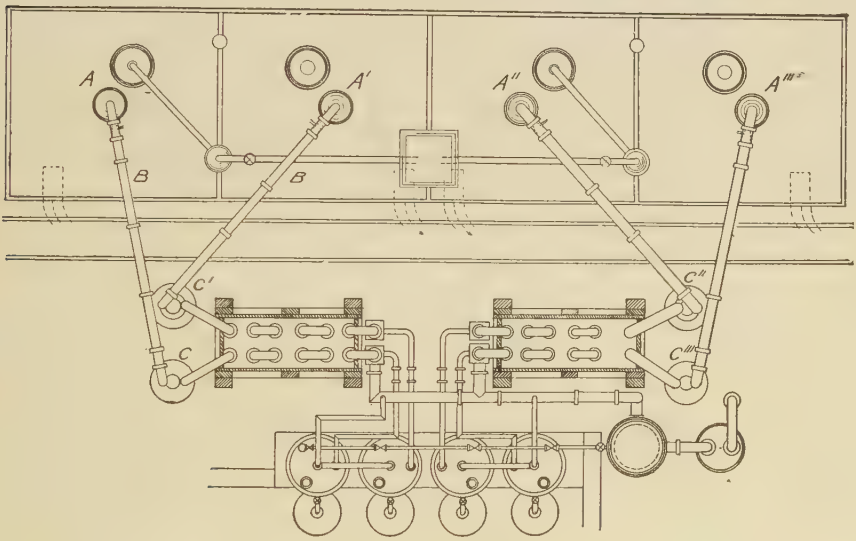


FIG. 110.

into the final receiver for bleached acid X. This system will seem to be somewhat complicated, but it is found to be thoroughly efficient and lends itself readily to careful control to the quality of acid at various points. Some of the larger manufacturers of strong nitric, for use in making mixed acid, both in this country and abroad, use this system, with great success. From 94 to 96 per cent recovery of the nitric from nitrate of soda is made and the average strength of all acid produced returning weak acid from the receiver Q into retort A along with the sulphuric acid used, is about 88 to 89 per cent without special drying of the nitrate of soda and using sulphuric acid of about 98 per cent before dilution with the weak nitric.

Gutmann Condenser. Somewhat similar in principle though less complicated in arrangement is the condenser system of Gutmann illustrated in Fig. 110. Here the gases from the stills A, A', etc., are taken over through the long stoneware pipes B, to preliminary receivers C, C', etc., similar

to those used in the plant just described. These serve a similar purpose, i.e., to catch any suspended or entrained matter that may be carried

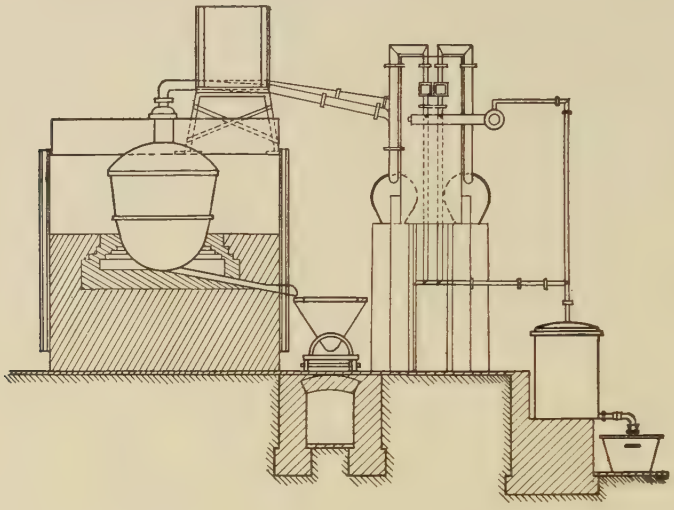


Fig. 111.

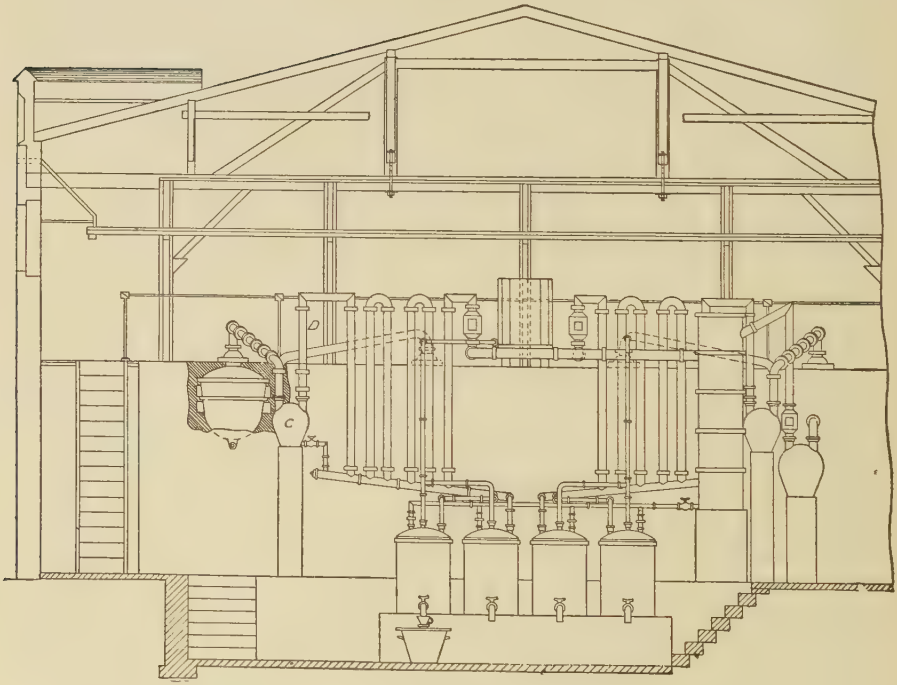


Fig. 112.

over by foaming or by excessive violence of gas evolution. Fig. 111 shows a side view of the same plant and Fig. 112 an end elevation. As

will be seen in the side view the receivers *C* are in this case also connected with the general acid line to the finished acid receivers so that if the acid collected in the receiver *C* proves of satisfactory quality it can be run in with the rest of the production from the plant. From this receiver the gases pass up through the pipe *D* into a series of vertical earthenware pipes set in water in a wooden tank. The joints are made just above the surface of the water and just below the bottom of the tank. The pipes passing out through slightly tapered holes in the bottom being surrounded with heavy rubber rings, stand down into the hole so as to make a water-tight joint. The water in this tank is maintained slightly warm and by proper manipulation a well bleached acid can be obtained. The gases after passing through these water-cooled pipes unite in a general gas main which conveys them to the final recovery tower, which is sprayed with acid from a receiver, not shown in the drawing, in a manner similar to that described in the previous plant. Here, however, only one tower is customarily used and the weak acid made is not as strong as that obtained in the other installation. Lanterns are provided for observing the color of the gases and controlling in this manner the draft of a chimney connected to the pipe through a final receiver intended to catch any last traces of suspended acid coming over from the splash of the distributor in the tower. The yield from the Gutmann plant is excellent and substantially all the acid is made in a ready bleached condition, but the securing of this result requires somewhat careful manipulation of the cooling water, and where there is no chamber plant to receive the weak acid made in the tower it is desirable to have two towers in series, so as to produce the weak acid of somewhat higher strength that can be used to better advantage in mixing with the sulphuric supplied to the retort. An injector is inserted in the gas pipe between the still and the first receiver and supplied with compressed air heated by passing through pipes set in the brickwork. This hot air serves two purposes: First, to quickly draw the gases away from the still and so far as possible shorten their contact with the hot iron, and in the second place it supplies the necessary oxygen to carry on a considerable amount of oxidation of the lower oxides of nitrogen in the pipes *B*, the receiver *C* and the warm condensing pipes immersed in the tanks.

Skoglund Condenser. In most nitric acid plants the aim is to combine the condensation and bleaching into a single step, by doing the condensation at such a temperature that as little of the lower oxides of nitrogen shall be condensed with the acid as possible and that in the second place what little is condensed shall be supplied with sufficient hot air to carry out its oxidation at once and produce in a single step a water-white acid of high strength. The simplest, and in the writer's opinion the most efficient, apparatus for this purpose is the condenser system of Skoglund, see Fig. 113. It is characterized by the carrying out of this preliminary condensation and bleaching action in a tower somewhat

similar to, though smaller in size than the final towers used for the oxidation of lower oxides that cannot be condensed. From the still A the gases pass over in the usual manner into a tourille or jar B, serving as a sort of safety bottle to catch any suspended matter that may be carried over when the still foams. From here they pass through a pipe C into a special injector pipe D which is arranged to be served with compressed air and thence into the bottom of the tower F. This tower is filled with lumps of quartz through which the hot gases mixed with air pass upward, while the acid, after condensation, flows downward. From the top of the tower the gases pass through a condenser which is generally a water-cooled coil. In this figure it is shown as an air-cooled series of pipes G which may, however, be water cooled if desired by covering each with a piece of linen and trickling water down upon them from above. The purpose of the linen is to distribute the film of water equally over the surface of the pipes and not permit it to flow through certain lines caused by salt deposits, thus producing irregular cooling and consequent breakage of the pipes. From this condenser the gases pass over by a pipe F to the bottom of the tower H and thence through the tower H', both of which are similar to the final towers in either of the other systems described, The acid produced in the condenser G flows downward through the tower. entering it at almost the boiling-point, which temperature is maintained throughout its entire flow over the surface of the quartz. Accumulating at the bottom of the tower, the acid then flows out through the pipe I into the small jar or tourille J, whence it flows through the cooling worm K, out of the top of this worm through the overflow L and into the final storage jar M. Similar storage jars are provided for the acid from the towers H and H' so that it may be returned with the sulphuric acid into the still A. Through the center mouthpiece of the jar J another hot-air pipe is carried to the bottom of the acid in J and the large mouthpiece of J is connected with a similar inlet to the tower so that instead of using the injector through the pipe D air is preferably blown through the hot acid collected in the jar J and the gases thus removed carried back into the tower. In order to maintain this tower at a high temperature it is customary to connect 3 or 4 stills charged in rotation to a single tower. Eit er the bottom of the tower is provided with inlets on three or four sides, or else a common gas main is employed, into which the injectors D are connected. The jar B is asbestos-covered but it cools down consider-

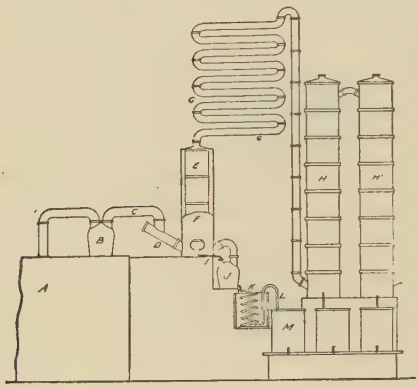


Fig. 113.

ably after each charge and serving as a sort of preliminary condenser to catch the first weaker acid that comes over when the still is charged. In some cases this acid is added to the condenser acid at the top of the tower by means of a specially provided neck, but generally it is mixed with the sulphuric acid and the weaker acid from the final towers H and H', the whole being returned to the still with the nitrated soda of the succeeding charge. Using moderately dry (not specially dried) nitrate of soda and 98 or 99 per cent sulphuric diluted with the weak nitric acid to a strength of approximately 93 per cent H_2SO_4, the average output from this plant is from 89 to 90 per cent in strength, perfectly water-white and substantially free from chlorine. The operation is conducted under a slight suction. As the tower E is carefully jacketed with insulating material so as to maintain its high temperature and protect it from contact with the cold air, and the pipes C and D are also carefully jacketed, there is practically no risk of breakage except of the air-cooled pipes G. This breakage is as small as can be credited to any form of nitric condensation.

Contact Process. One marked development of the war has been the production of nitric acid by the oxidation of NH_3 gas, passing it mixed with air over contact materials and absorbing, oxidizing and concentrating the oxides of nitrogen produced. Direct oxidation of the nitrogen in the air by burning it in the electric arc has proven too expensive even for war purposes except in the few locations having very cheap waterpower (about half the price of power at Niagara Falls). But synthetic production of ammonia from hydrogen of water and nitrogen of air has been perfected by the cyanamid process and by the Haber direct synthesis over a contact mass under high pressure, until either system is capable of producing NH_3 gas at a cost of about 8 cents per lb. This permits the production from the NH_3 of HNO_3 by a process very similar to the contact process of making sulphuric acid, and at a cost approximating 4 cents per lb. The development of this branch of the nitric acid industry in this country is, however, still in too much of a transition stage to be described in detail here.

Storage and Packing. Nitric acid is stored in stoneware pots or in the carboys to be shipped. For the manufacture of mixed acid, however, it is most conveniently stored along with a portion of the sulphuric acid with which it is necessary to mix it. When containing 5 per cent of sulphuric acid and not over 3 per cent of water, the mixture may be quite safely stored in iron tanks for an indefinite period. Iron is much preferable to lead for strong acid, while stoneware is better than either for weaker acid. The carboys used for the shipment of nitric acid are usually not packed with hay because of the risk of fire should a carboy be broken and the strong nitric acid come in contact with the organic material. The rubber-packed carboys described under the chapter on sulphuric acid are much preferable for nitric acid.

CHAPTER VI

SALT, HYDROCHLORIC ACID, AND SODIUM SULPHATE

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Salt. Common salt has been known and used since the time of the earliest man. It is an important constituent of food for both man and animals. It is found in all parts of the world. Small amounts are present in most river waters, and some spring waters are impregnated with large quantities of it. Sea water contains it to the extent of about 3 per cent, while the water of the Dead Sea contains about 10 per cent, and that of the Great Salt Lake, 9.7 per cent. It is also found in large deposits as rock salt, where it may exist in a colorless, transparent form or with varying grades of purity down to a marl-like mass which contains but little salt. The deposits that are worked usually consist of salt not in transparent condition, but in a white, gray, or red massive state. When it is transparent it will split out in cubes, but there is no cleavage in its more impure conditions. There are many deposits of rock salt in Germany and Austria, the most important being at Stassfurt. In Spain there is a bed of importance; and in fact all countries possess some salt deposits. The United States leads all countries in the production of salt, furnishing in 1912, 33,334,808 barrels of two hundred pounds. Of the various States Michigan produces the largest quantity; in 1912 this State furnishing nearly 11,000,000 barrels. While the output of New York is over 400,000 barrels less than that of Michigan, the quality makes it much more valuable. The value of the 1912 production was $2,597,280. New York has led, as far as value goes, for the last five years. Louisiana leads in the production of pure rock salt, but important workings are also found in Kansas, Colorado, and other States. An immense body of salt underlies the whole of central Kansas, the exact extent is not definitely known. It varies in thickness from a few feet to over 400 feet. The deposits are not pure salt, but layers of from a few inches to 20 feet in thickness alternate with layers of rock consisting of shale, limestone, and gypsum. The salt itself is from 96 to 98 per cent pure. The layers are uniform in composition, but different layers vary greatly in purity. The lower layers contain much gypsum, while the upper portion is quite dark in color. These deposits are not worked to the limit as the market does not demand it. The product is as a rule used without purification.

Rock salt and brine, with few exceptions, contain so much impurity that for the table and for many manufacturing purposes the salt must be purified before use.

Properties. Sodium chloride is a colorless, crystalline solid, with a specific gravity of 2.13, crystallizing in cubes often with hollow faces. It melts at 815° C. or 1500° F., and volatilizes below a white heat. There is little difference in the solubility of salt in hot and cold water, 100 parts of water at 0° dissolving 36 parts of salt, while 100 parts of water at boiling temperature dissolve 39 parts. This fact makes it possible to separate salt from its impurities, as most other substances are much more soluble in hot than in cold water. Absolutely pure salt is not hygroscopic, but ordinary salt will attract moisture from the air, sometimes in quantities sufficient to form a paste. This is due to the presence of admixed calcium or magnesium chloride, which always accompanies salt in its deposits.

Theory of Deposits. The salt beds always give indications of being the result of the drying up of salt seas. In these deposits the admixed salts are found in the relative order of their solubility. On the bottom are found the insoluble calcium sulphate, calcium and magnesium carbonates, while on the top are the deliquescent chlorides of calcium and magnesium, with the chlorides of sodium and potassium and their sulphates and the sulphate of magnesium intermediate in the order of their solubility. In the Stassfurt deposits sixteen different salts may be recognized. The problem of producing commercial salt is to separate it from its impurities, and this is done usually by recrystallization.

Working of Deposit. The working of the salt deposits is dependent upon the purity. In Germany, Louisiana, and many other deposits the salt is mined. Shafts are sunk and galleries are run, often a mile or more in length. The salt is under cut and then blasted down from above with low-power dynamite. The broken-down mass is taken to the mill and run between corrugated rollers. The crushed salt is screened to various sizes, the finer grades being blown to remove the dust. One Colorado deposit is in the form of a crust over an underground lake of brine. In working this deposit the earth is removed and the salt cut like ice, washed in the brine, and then crushed. In other deposits, as in New York and Ohio, the location of the bed, or the large quantity of admixed clay or earthy matter, renders this method impractical, and the salt is removed from the ground by boring wells, dissolving out the salt with water, and pumping to the surface by turbines forced down to the bottom of the pipe. In this case it is important to protect the upper part of the wells with pipes to prevent the absorption of the brine by the surface soil. The brine, whether natural (sea water, spring water) or artificial, must now be concentrated. This may be done either by natural evaporation through the aid of the sun or by the use of fuel. A means of purifying both rock salt and brine in one process consists in saturating the latter with the former and then crystallizing. In warm countries,

as along the shores of the Mediterranean and in California, the sea water is collected in reservoirs and then exposed in shallow basins to the heat of the sun, the salt being removed as it crystallizes, placed in heaps, and allowed to drain and dry. One plant in California, covering 600 acres, divided into seven basins, requiring 15 miles of levees, produces 2000 tons of salt a year. Ponds, protected by tide gates, are flooded from the ocean at high tide every two weeks. The water is pumped into secondary basins where the level is maintained constant for two weeks. It will reach the concentration of 1.04. In a second set of ponds the bulk of the calcium carbonate and gypsum will be deposited. In the next series of basins the crystallization takes place. When the density of the brine reaches 1.15, it is run into the "bittern" pond. If the brine is allowed to concentrate above 1.15, potassium and magnesium salts will be deposited. Very little use can be made of the salts in the bittern. When the ponds are drained a layer of 7 to 8 inches of salt will remain, this is at the rate of about 110 tons per acre. The season is from May to October. This is so impure that it must be refined before it can be used for table or dairy purposes. A process similar to this is practiced in working the salt in Great Salt Lake. The water is pumped into crystallizing ponds, which are simply large areas enclosed with mud banks about 2 feet high and divided into smaller basins. The total area of these ponds is about 2 square miles. The crystallization is carried on from March 15th to September 15th, after which time the liquid " bittern " is run back into the lake and the " crop " gathered. The " crop " consists of a layer of about 6 inches of salt, or about 90 tons per acre. The brine, which was run back into the lake, carries with it the bulk of the impurities, particularly the calcium and magnesium salts, but the gathered salt is largely contaminated with sodium sulphate. This impurity is removed by drying, when the sulphate will effloresce and be reduced to a fine powder. When this powder is acted upon by a current of compressed air, the fine sulphate will be blown away, leaving the coarser salt. When this is ground and screened, it contains about 98 per cent of sodium chloride. The fine material which was blown out contains about 75 per cent of salt; this is pressed in cakes, and is used for cattle and sheep. This salt is not very satisfactory for dairy purposes, owing to the sulphates which it still contains. In Norway and other cold countries the sea water is concentrated by freezing the water in enclosed basins, then pumping out the still liquid part, which contains all of the salt, and evaporating to crystallization.

Purification of Salt. For the production of table salt some form of purification must be given to most natural salts. This purification may be of the solid salt or the brine. A method used in the purification of solar salt consists in washing by means of brine. The brine flows through a narrow box and the solid salt is carried through by means of a screw conveyor. It is then washed by spraying first with sea water and

then with fresh water. The washings are returned to the process. This same method is used to purify rock salt, using a solution of pure salt in pure water for washing. This method will not remove any sulphates that may be present in the rock salt.

An English method is used abroad to some extent. This consists in melting rock salt and forcing air through the molten mass which is maintained in a state of quiet fusion for some time. The molten salt is then allowed to flow over a dam into a second chamber and then into a revolving cooler where it will solidify. The main operation in this process is the settling after oxidation. This method has not come into use in this country but is quite common in Ireland.

Brines are treated chemically to precipitate the calcium and magnesium salts which are the chief impurities. Soda ash and lime, or soda ash and caustic, are added to the brine which is then run into settling tanks. Occasionally some barium chloride is added to precipitate the sulphates. This treatment must precede the soda addition.

A more modern method consists in electrolyzing a portion of the brine producing some sodium hydroxide, carbon dioxide is blown through the solution, thus producing carbonate. This solution is then added to the raw brine whereupon the iron, calcium, and magnesium will be precipitated; these are filtered out and the solution evaporated.

The impurities found in ordinary salt and brines, while imparting an objectionable color and a bitter taste to the salt, are not of a markedly deleterious character as to the food value. Salts of barium do not belong to this class, and salt deposits and brines containing this metal have not been looked upon as having any great value. It is true that this salt has been marketed plainly labeled "not to be used for food," or "do not feed to stock," but numerous cases of poisoning have been reported and the cause directly traced to the presence of barium. Many of the brines of the Ohio valley contain barium to a considerable extent; great care must be exercised in the purification, and large quantities of "off grade" salt are collected. Recently a method has been developed for the removal of barium from brines and the production of a high grade salt from the impure raw material. The method consists in adding sodium sulphate in quantity 30 per cent in excess of that required to balance the barium. Unless this excess is taken, the barium is not completely precipitated, and, if too much is taken, the calcium sulphate will be deposited in the form of a hard insulating scale upon the steam pipes. Not only does the sulphate treatment remove the barium, but it also aids in the removal of the iron, which will be deposited in the form of a sludge with the barium sulphate.

In some places the "bittern" is of no value, but in other localities it forms an important source of bromine and magnesium salts.

Evaporation of Brine. The usual form of apparatus for evaporating the brine by artificial heat is a long, narrow, shallow pan, heated at one

end and with flues running the entire length. These pans vary from 40 feet to over 100 feet in length and from 10 to 25 feet in width. The salt is raked out as it forms. The most difficult impurity to remove here is calcium sulphate, which collects in the form of a scale on the pan. This must be removed or local superheating will result in the destruction of the pan. Various attempts have been made to use the vacuum pan in the salt-boiling industry, but, on account of the separation of anhydrous calcium sulphate, this process can not be used with all brines. In many plants multiple effect vacuum pans are used. As a rule triple effect is the most satisfactory, and can be used only after the brine has been purified. Another objection to the use of vacuum pans for raw brines is the violently corrosive action upon the pipes due to the free acid formed by hydrolysis of the magnesium salts. For other grades the " grainer " is used. The grainer is a long shallow tank containing 3-inch steam pipes. The older types were raked by hand, but the newer types are constantly raked by mechanical rakes, which agitate the liquor and produce much smaller crystals. In the boiling of salt, if a small quantity of fat or oil is added to the pan, it prevents the formation of a crust on the surface, which would retard evaporation. The salt which is *fished* out of the pans is exposed to steam. This dissolves out the more soluble chlorides of calcium and magnesium, after which it is *whizzed* and dried.

Uses of Salt. In addition to its use for table and dairy purposes, sodium chloride is used in preparing sodium sulphate, sodium carbonate, and indirectly for the production of all sodium salts. It is used in tanning, wet extracting of copper and silver from ores, as a glaze for common earthenware or stoneware, and as a food preservative. Hydrochloric acid is also produced from common salt.

Grades of salt are numbers 1, 2, 3, 4, C fine, packer's fine, and lump. No. 1 is most used,—grains about $\frac{1}{8}$ inch; No. 2, grains $\frac{1}{8}$ to $\frac{1}{4}$ inch; No. 3, over $\frac{1}{4}$ inch; No. 4, coarse evaporated; C fine is from No. 1 down.

No. 1 and C fine are used for salting hides, soap making, salt cake, caustic, freezing brines and freezing mixtures. No. 2 is sold largely to packers and used for freezing mixtures; No. 3, in refrigerators; No. 4 and lump, for stock feeding.

Some countries impose a tax on salt used for table or dairy purposes; commercial salt being prepared under government supervision and " denatured " by the addition of various substances which would render it unfit for table use, such as Glauber's salt, soda ash, 4–15 per cent, soda crystals, 12 per cent, sulphuric acid, 2 per cent, strong hydrochloric acid, 2 per cent, ammonia liquor, or aniline dye. The use to which the salt is to be put determines the denaturing substances.

Sodium Sulphate. Sodium sulphate occurs in nature both in crystallized form and dissolved in water. Large deposits are found in Arizona, Spain, Peru, Hungary, Siberia, and Hawaiian Islands. Some salt works evaporate the bittern for the production of sulphate, but this is as a

rule contaminated with much magnesium. Much of this sulphate is pure enough for technical uses. Nearly all natural sulphate, however, contains enough iron to make it unfit for glass manufacture. As a usual thing sodium sulphate is prepared in the anhydrous state, and only a small proportion is converted into the crystallized form.

The usual method of preparing salt cake is by the action of sulphuric acid upon salt, producing hydrochloric acid as a byproduct. In this country, where the Leblanc soda process is not used, hydrochloric acid is made, and the sulphate obtained as a byproduct.

In the manufacture of nitric acid by the action of sulphuric acid upon soda nitre, the sulphate formed is $NaHSO_4$, which is of very little technical use. In most places this is considered a true waste product and treated as such. If vitriol and nitre were taken in the proportion required to produce a neutral sulphate, the extra cost of working and the loss by decomposition would more than balance the value of the sulphate formed. In England it is customary to mix the nitre cake with the salt in the salt cake furnace and work it up in that way. This is done in some places in this country and the practice is growing. Mechanical furnaces must be used in this process. Many other methods have been proposed for making sulphate, but the only one to meet with success is that of Hargreaves and Robinson, which has been used to some extent in Europe since 1870, but finds in this country limited application, due largely to the fact that Leblanc soda is not made here. This method consists in passing sulphur dioxide (burner gas), oxygen (air), and steam, over salt, whereupon decomposition takes place:

$$2NaCl+SO_2+O+H_2O=Na_2SO_4+2HCl.$$

The salt must be specially prepared, so as to make it porous and thus easily penetrated by the gases. This is done first by grinding the salt, then mixing with sawdust or coal and water, moulding into a cake, and drying between plates. The decomposition takes place in cast-iron cylinders arranged in a battery of eight, six of which are in use while the other two are being recharged. The principle of the counter currents is used here, the fresh salt being acted upon by the gas almost exhausted, and the fresh gas coming in contact with the almost converted sulphate. The gas should be in the ratio of 2 sulphur dioxide, 2 steam, and 1 oxygen. A temperature of 400° must be maintained. The yield is from 93 per cent to 98 per cent. Hargreaves' method is not satisfactory unless it can be worked on a large scale.

By far the most important method for the production of sulphate is the old method of decomposing salt with sulphuric acid. This decomposition takes place in two stages: first, $NaCl+H_2SO_4=NaHSO_4+HCl$; second, $NaCl+NaHSO_4=Na_2SO_4+HCl$. The first of these takes place at ordinary temperatures, but the second requires considerable heat. The actual decomposition is usually accomplished in two parts of the furnace, except

where the cylinder furnaces are used. Here the operation is complete in the one apparatus. The salt and sulphuric acid are mixed in a cast-iron pan, and gently heated, usually by waste heat, until the mass becomes stiff. It is then pushed over onto the bed of a reverberatory furnace, where it is heated until all the acid is driven off. In many works, instead of the reverberatory furnace, a muffle keeps the acid vapors and the furnace gas separate, and prevents contamination of the sulphate with the furnace dust, thus permitting the use of coal instead of coke for fuel. During the second heating the mass is worked by rakes and slice bars in order to insure complete action.

Formerly the pans were made of lead, but they have almost entirely been replaced by cast-iron pans. The lead pans are still used in making salt cake for the plate-glass industry. The iron pans are circular in shape, from 10 to 14 ft. in diameter, and about 2 ft. deep (Fig. 114). They are, at the bottom, 5 to 7 ins. thick, and on the sides, 2 to 7 ins. They are built in the furnace and covered with a gas-tight dome of firebrick, and provided with an earthenware pipe to carry away the hydrochloric acid. Mechanical salt cake furnaces have been introduced in England, but they are objected to on account of the introduction of a considerable quantity of iron into the salt cake. These furnaces consist of flat-bottomed iron pans, provided with a shaft carrying plows to keep the mass thoroughly worked up. When the reaction is complete the salt cake is raked out and allowed to cool.

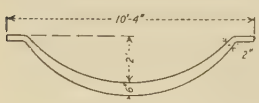

Fig. 114.

Salt cake contains from 93 to 99 per cent of Na_2SO_4. The varying quantities of impurities in salt cake, such as $NaHSO_4$, $CaSO_4$, $FeSO_4$, Fe_2O_3, $MgSO_4$, SiO_2, NaCl, depend upon the salt used and the kind of furnace. The sulphate from Hargreaves' process gives a purer product, except that its content of NaCl is high.

Glauber's Salt. In the production of Glauber's salt, the salt cake is dissolved in hot water, filter pressed, and run into coolers. If the salt is desired inlarge crystals (to adulterate crystal soda), the coolers are made of heavy planking and so protected that the cyrstallization takes place without any agitation. If from 10 to 12 per cent of soda is added with the salt cake, the crystals will be larger, firmer, and more like soda. If small granular crystals are desired, the hot liquid is run into large coolers, and when the temperature has fallen to about 30° C., the liquid is agitated either by a wooden paddle or by blowing compressed air through it; this yields the sulphate in the form of fine needles, much resembling Epsom's salt; and it was formerly used to adulterate and even as a substitute for that salt. The addition of some soda ash before crystallization serves the double purpose of improving the appearance of the crystals and precipitating the iron. A little milk of lime is also added to free it from iron adulteration.

In order to get a very pure Glauber's salt, the crystals first obtained are freed from the mother liquor by *whizzing*, and are recrystallized. The crystallizing of a batch of sulphate crystals takes from five to eight days in winter, and from fifteen to twenty days in the summer. The great change in the solubility, due to a slight change in temperature, makes it more profitable to push the crystallization during the winter and store up the material during the summer.

The principal uses of sodium sulphate are soda making, glass making, especially window and bottle glass, and for making ultramarine. In the form of Glauber's salt it is used as a mordant, in the production of thiosulphate, in medicine, especially for veterinary uses, and in the making of cooling mixtures.

Hydrochloric Acid. Hydrochloric acid occurs in nature as a constituent of volcanic gases, and is also found dissolved in water. Some of the head streams of the Amazon and other South American rivers have small quantities, but with no commercial value. In the manufacture of hydrochloric acid, a chloride, either a natural salt or a waste product from some industrial operation, is used.

Numerous patents have been taken out for apparatus to burn a mixture of hydrogen and chlorine. This has not met with any application as yet. The method may be used in the future with electrolysis of brine as the source of the gases and caustic as a side product. At the present time, however, chlorine and bleach are of more value than the acid.

Various patents have also been taken out to act upon hydrocarbons with chlorine, but they have not been used.

This acid was known to the ancients only as a solution and was made by them by fusing salt with green vitriol. The gas was not known until the time of Priestly. In the early days of the alkali industry the hydrochloric acid, a waste product formed in the production of sulphate, was a great nuisance and caused the manufacturer trouble by destroying vegetation for some distance around the plant. To prevent this, they built stacks 500 ft. high so as to dilute the acid vapors; but this only served to widen the circle of destruction, which extended over a mile and a half from the works. Then they conducted the gas into underground cisterns and channels, absorbing the gas in water and discharging it into the nearest water course. This killed the fish and gave an acid water which would corrode the metal parts of ships. Then came the economic absorption by water and the utilization of the acid formed in the production of chlorine, which was consumed in the bleach manufacturing industry. Thus, the production of bleach was a natural outcome of the alkali industry, utilizing the waste acid from the salt cake apparatus. In this country hydrochloric acid is the principal product of the action of sulphuric acid on salt, and the sulphate is of secondary consideration. In England the method of condensation is by the use of coke towers, the acid vapors rising through a tall narrow tower packed with coke, and

meeting a stream of water which flows down from the top. In Europe a series of earthenware Woulff bottles (bombonns, Fig. 115) is used. In this country a combination process has been generally employed, the gas first passing through a train of the Woulff bottles, and then into a coke tower. The water, which enters the top of the coke tower, flows through the Woulff bottles, and the strong hydrochloric acid is collected from the first bottle. Often, fifty or more bottles being in the series, the acid liquid bound from one bottle to another through overflow connections half way up the bottle, the connections being made with glass tubes, which discharge into the bottom of the receiving bottle. As the gas should be as cool as possible before it enters the condensers, long cooling pipes are introduced between the furnaces and the condensers.

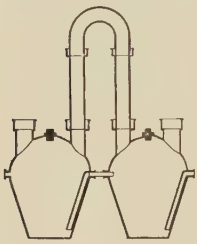

Fig. 115.

In recent years the "Cellarius Tourills" (Figs. 116 and 117) have replaced the Woulff bottles in many factories. The especial advantage here is the relatively large surface exposed for the quantity of liquid used. These tourills may be immersed in cooling water, thus increasing the efficiency by reducing the temperature. As the concentration of hydrochloric acid is a function of the temperature of the absorbing system, any apparatus aiding in the dissipation of the heat of absorption will increase the efficiency. In using this system the first two tourills (Fig. 118) are empty and act as coolers and condensers for the sulphuric acid which may have been carried over.

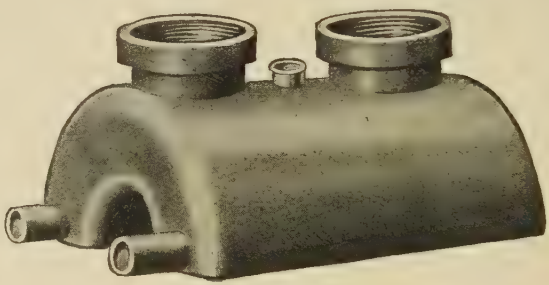

Fig. 116.

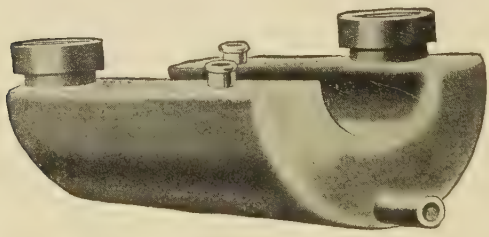

Fig. 117.

In some works it is the practice to introduce a small quantity of fat or oil into the decomposition chamber to prevent frothing. This fat may be carried over by the acid fumes, form a layer upon the surface of the water, and thus prevent absorption. The removal of this fat is another use of the empty tourills. A tower packed with brick or some surface exposing substance is frequently placed between the furnace and the absorbing system for the purpose of removing the insoluble matter by surface condensation. This gas filter

should not be too close to the furnace, but should be allowed to act upon the cooled gas, preferably after the cooling tourills.

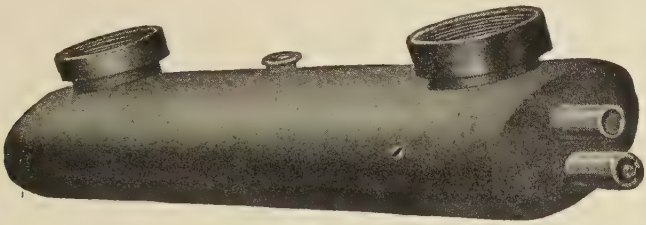

FIG. 118.

It has been the practice to use the same form of absorbing system for both the pan and muffle gas, notwithstanding the fact that there is a vast difference in the concentration. A quiet, extended surface is very satisfactory for the rich muffle gas, but not so efficient for a more dilute gas. In any case, at the end of the system a dilute gas must be treated. The tower system has been generally used, but a more recent method consists in bringing the dilute gas into a chamber filled with a fine spray or mist. In this way we have maximum contact between gas and liquid, but there is the increased cost of pumping and producing the spray. It is proposed to entirely substitute the spray apparatus for the other forms of absorbing apparatus, retaining only the cooling tourills. The material from which the apparatus is made has a marked influence upon the efficiency of the plant. (T. Meyer, Zeit. angew. Ch. 26, p. 97.)

In the description of the production of sulphate by the action of sulphuric acid upon salt, mention was made of the fact that the reaction takes place in two stages—first in the cold from the pan, and second in the furnace proper. The hydrochloric acid which comes from the furnace is not as pure as that formed in the pan, and, as a rule, the two acids are run through separate condensing systems, and the resulting solutions collected separately and sold as different grade acids. That coming from the roaster will contain more iron, sulphuric acid, arsenic, and other impurities than the acid collected from the pan. Hydrochloric acid is rarely distilled, the pure acid being made from pure materials.

Occasionally it becomes necessary to purify hydrochloric acid. Barium sulphide is used; this removes both arsenic and sulphuric acid. The acid may be purified by allowing the crude acid to fall into hot concentrated sulphuric acid or fused magnesium chloride. Le Roy (Chem. Trades Jour., 1913) proposes to pass the gas through a pipe surrounded with chilled brine, thus condensing the arsenic, iron salts, sulphuric acid, and all impurities carried over.

Very many attempts have been made and patents taken out for the conversion of hydrous magnesium chloride into hydrochloric acid and magnesia by the application of heat, the equation $MgCl_2+H_2O=MgO$

+2HCl being usually given to express the change. So far all these attempts have proven successful only in part. The temperature required, the cost of labor in removing the residue from the furnace, and the fact that the reaction does not take place as written, but with the formation of an oxychloride which has little or no value, makes the process still imperfect. It is found to some extent in Germany, where the naturally occurring chloride is utilized.

Purification. Manufacturers have found it more profitable to make pure acid from pure, new material than to purify crude acid. Sulphuric acid is removed by adding to the acid, as it comes from the absorbers, ground barium carbonate, allowing to settle, and then decanting. Arsenic is removed by washing with coal oil in a tower between the furnace and the absorbers. Another method of purification consists in running the crude hydraulic acid in a thin stream into hot vitriol. The gaseous acid driven out is passed through lead pipes and absorbed in pure water running through lead towers packed with pure quartz or well-washed coke. The sulphuric acid, being concentrated by heating, can be used over again.

Uses of Hydrochloric Acid. Hydrochloric acid is used in "pickling" iron for tinning, in the making of chlorides and of chlorine, in the production of glue, in the preparation of fatty acids from the lime soap, and for various other purposes.

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CHAPTER VII

ELEMENTS AND COMPOUNDS

ALLEN ROGERS

Aluminium. This is one of the most important of the elements. It occurs in nature in the form of hydrated oxides, such as *bauxite, diaspore,* and *hydrargillite;* and of silicates, such as *common clay, kaolin, feldspar,* and *cryolite.* It was first prepared in a free state in 1827 by Wöhler, who heated to redness a mixture of aluminium chloride and metallic potassium. Many attempts were made to produce the metal electrolytically, but they were not successful in America until 1890, when Hall took out his patents on the electrolysis of fused alumina in the presence of a fluoride. The raw material for this purpose is bauxite, obtained mostly from France, and its purification is a very essential and important factor in the economical production of the metal. The process is described in Chapter IX.

Aluminium is a silvery white metal of specific gravity 2.7. Its lightness and resistance to atmospheric influences have brought it into use for a variety of purposes where great strength and low weight are desirable. Alloyed with other metals, aluminium gives a valuable series of bronzes, some of which possess great tensile strength and resistance to corrosion. A finely divided form of metallic aluminium is used in flash-light powders. As a war material, aluminium is useful for time fuses, flash-light-tips of rifle bullets, star shells, machine-gun radiators, airplanes, and even in the explosive "ammonal," consisting of powdered aluminium with ammonium nitrate. In automobiles, it is a necessity; while its use in cooking utensils has made it a household friend.

The application of aluminium to what is known as the *Thermit Process* for welding and foundry practice is important and depends on the fact that aluminium will take up oxygen from oxides when heated with them. Dr. Goldschmidt discovered that this reaction could be controlled and that, at the end of it, he had aluminium oxide as slag floating on top in a molten state, the reduced metal remaining at the bottom of the container. Thus, in making a thermit weld, the parts to be united are first arranged with a space between them varying from $\frac{1}{2}$ inch to 2 or 3 inches, depending upon the size of the sections. Where the pieces to be welded are in two parts, it is a simple matter, of course, to provide this space, but in the case of a fracture, it is often necessary to cut out the steel in order

to provide the space needed, and this is done either by drilling a line of holes along the fracture and then cutting out the metal between the holes, or by cutting the space out with the oxy-acetylene cutting flame.

In the case of welding locomotive frames, which is the most important application of the process, it is almost always necessary to cut out the fracture. After the sections have been cut out, there is formed a wax pattern shaped exactly like the reinforcement of thermit steel that is to be cast around them to make the weld. Thermit is a mixture of aluminium and iron oxide, which react when ignited. The aluminium combines with the oxygen of the iron oxide, while the iron is set free and comes down as a highly superheated liquid steel at a temperature of nearly 5000° F., or about twice the temperature for ordinary molten steel. It will be readily seen that if this steel is poured around the sections to be united, it will melt them and amalgamate with them, so that the whole will cool down to form a single homogeneous mass.

The process is a simple one, and the only outside power required to weld sections of any size is a small supply of compressed air for the operation of the preheater. The outfit is entirely portable, and in many cases sections of very large size are welded without removal from their position, and therefore with a greater saving in time and expense than when obtaining new parts or repairing by other means.

Aluminium Oxide. The oxide of aluminium is of commercial importance in the form of *corundum*, *emery*, *ruby*, and *sapphire*, and also as a raw material for making metallic aluminium.

Aluminium Acetate. This compound, usually found on the market in a liquid condition known as "red liquor," may be prepared either by action upon aluminium hydroxide with acetic acid, or by double decomposition of aluminium sulphate with calcium acetate. It is principally used as a mordant in dyeing and printing and in the water-proofing of fabrics.

Aluminium Chloride. This compound is prepared by passing dry hydrochloric acid gas over heated metallic aluminium, or by heating a mixture of aluminium oxide and carbon in the presence of chlorine. The chloride distills off as a white crystalline mass, which fumes in the air and boils at 183° C. Its principal use is in the manufacture of organic compounds by the Friedel and Craft reaction. Its acid solution is sometimes used as a disinfectant. The chemical is also essential in some of the processes for cracking oils.

Aluminium Hydroxide. This product is obtained as a gelatinous precipitate on treating salts of aluminium with alkaline hydroxides or carbonates. On a commercial scale it is usually prepared by the Löwig process, which consists in treating sodium aluminate with milk of lime. The freshly prepared aluminium hydroxide precipitates many of the dyestuffs from their solutions, thus forming insoluble colors known as *lakes*.

Aluminium Sulphate. The sulphate of aluminium, $Al_2(SO_4)_3 \cdot 18H_2O$, is prepared from clay, bauxite, or from the aluminium oxide obtained in the manufacture of soda by the cryolite process. The calcined clay is finely pulverized and treated with sulphuric acid (sp.gr. 1.47). The mixture is heated to start the reaction, which soon becomes violent leaving a hard cake (alum cake) which contains silica, iron, and other impurities. From bauxite it is prepared by adding enough sodium carbonate to the finely powdered mineral to form a mixture containing 1.2 molecules of sodium carbonate for every molecule of aluminium oxide. The mass, after fusion, is rapidly lixiviated, and the solution of sodium aluminate thus obtained is filtered, concentrated to 35° Bé., and treated with a current of carbon dioxide which precipitates the Al_2O_3 in a granular form. This precipitated oxide, on dissolving in sulphuric acid, produces a very pure form of aluminium sulphate, which contains not over .02 per cent of Fe_2O_3.

Potash Alum. Potassium aluminium sulphate, $Al_2(SO_4)_3 \cdot K_2SO_4 \cdot 24H_2O$, is obtained from alumite or alumstone, found mostly near Rome. The mineral is calcined at a moderate heat (about 500° C.), exposed, when moist, to the atmosphere for 3 or 4 months, and then lixiviated. The alum resulting from the evaporation of the wash waters contains a small amount of basic aluminium sulphate and crystallizes in cubes called Roman or cubical alum.

Alum may be obtained from alum shists or shales by roasting and subsequent exposure to the air. The iron sulphide present is oxidized to sulphate and sulphuric acid. The latter reacts on the aluminium silicate, forming sulphate of aluminium. The ferric sulphate formed attacks the aluminium compounds, producing aluminium sulphate and basic ferric sulphate. The mass is washed and the solution evaporated to 40° Bé. Most of the iron compounds crystallize out and are separated. The proper amount of potassium sulphate in concentrated solution is now added, and the alum begins to separate. The crystalline product still contains some iron and must be purified by recrystallization.

Alum may be readily made by adding the proper amount of potassium sulphate to a concentrated solution of aluminium sulphate and allowing it to crystallize out.

Alum, as well as aluminium sulphate, are used in dyeing, as mordants in the sizing of paper, in tanning, and in purifying water.

Sodium and Ammonium Alums. These alums may be obtained by using sodium or ammonium sulphate in place of potassium sulphate. All of them have nearly the same chemical and physical properties, being colorless, soluble salts that crystallize in octahedra.

Ammonia. When animal matter undergoes decomposition, more or less ammonia is formed; also when nitrogenous, organic substances are subjected to destructive distillation. For example, during the distilla-

tion of coal for the production of illuminating gas and coke, most of the ammonia of commerce is produced. To a limited extent, ammonia is also obtained from the distillation of bones and other animal matter, from a putrid urine, sugar residues, and waste furnace gas. It is likewise possible to get ammonia by passing air over a mixture of barium oxide and carbon heated to a white heat, but the process has never met with commercial success. Other electrolytic processes are described in Chapter IX.

The nitrogen in the ammoniacal liquor of the gas works is present in the form of free ammonia, ammonia combined as carbonate, sulphide, sulphydrate, sulphite, sulphocyanide, and ferro-cyanide. As the liquor comes from the hydraulic main, the scrubbers, and condensers, it is mixed with a large amount of tarry matter, which, on standing, settles out, leaving a fairly clear liquid that may be treated for its ammonia content. There are various methods for recovering the ammonia, but a most common one makes use of the Feldman apparatus: The settled gas liquor passes by means of a series of narrow tubes through a cylindrical chamber where it becomes somewhat heated from the waste gases passing through this chamber, known as the "economizer." The heated liquor is then forced to the top of a tall tower, where it meets a current of steam which causes volatile ammonia compounds to be liberated; when the non-volatile compounds flow down the tower and come into contact with boiling lime water, free ammonia is produced. The free and volatile ammonia compounds are next conducted through a large pipe into an absorption vessel containing sulphuric acid. Here the sulphides and other volatile salts of ammonia are decomposed with the formation of ammonium sulphate and the liberation of hydrogen sulphide and carbon dioxide. These hot gases are collected in the dome over the absorption vessel and from there pass into the shell of the economizer, producing the heat referred to above. The waste sludge from the lime treatment is drawn off at intervals, and the liquor in the absorption vessel concentrated as it becomes saturated, being sold as crude ammonium sulphate.

On recrystallizing the crude ammonium sulphate and redistilling with lime, a pure gas is obtained, which, being absorbed in water, forms the "aqua ammonia" of commerce, or the ammonium hydroxide of the laboratory. By subjecting ammonia gas to high pressure it is possible to convert it into a liquid. Liquid ammonia has extensive application at present as a refrigerating agent in ice machines.

The direct procurement of ammonia from its elements is at present a subject of the greatest importance from the standpoint not only of economy, but also of necessity. Although large quantities are being made by a direct union of nitrogen and hydrogen, the literature on the subject is very meager. One of the greatest problems involved in the production of synthetic ammonia is how to secure the elements in such a pure condition that they will not affect the catalytic agent used. The difficulties

encountered have been largely overcome, and now the simple question is which process will give the largest yield.

Ammonium Carbonate. The commercial product is prepared by heating a mixture of sulphate of ammonia and powdered calcium carbonate in iron retorts and collecting the sublimate formed in lead-lined chambers. The yield is ammonium bicarbonate and ammonium carbonate mixed.

Ammonium Chloride. This compound is manufactured either by absorbing the gas in dilute hydrochloric acid, or by neutralizing the gas liquor directly with the acid. In either case the resulting solution is evaporated for crystals, which are then purified by recrystallization or sublimation. Ammonium chloride is usually purified, however, by sublimation, in which case it is heated in iron or earthenware pots with dome-shaped covers. The purified product collects in the dome as a thick crystalline cake, which is removed and placed on the market as *sal-ammoniac.* Formerly this salt was made by burning dried camel's dung, but at present it is all prepared from gas liquor.

Ammonium chloride is used in soldering, in the manufacture of dyestuffs, and in calico printing. It also has extensive application in electrical appliances.

Ammonium Nitrate. This salt is prepared in a similar manner to the chloride, but it cannot be purified by sublimation. Its chief value is in the manufacture of explosives and of nitrous oxide, so-called *laughing gas.*

Ammonium Sulphate. The crude salt is dark brown in color, and its preparation is described under ammonia. Its main use is as a base for making other ammonia salts, and, in the impure form, for the manufacture of fertilizer. When purified, it gives a white crystalline substance used for fire-proofing fabrics and for other purposes.

Antimony. This element occurs in nature as the sulphide, *stibnite,* Sb_2S_2. The antimony sulphide is first separated from the gangue by heating in a furnace with sloping floor, along which the fused sulphide flows in a channel. This sulphide is then placed in a reverberatory furnace, where it is converted into the oxide. The oxide is heated in a crucible, and, on cooling, the metal settles to the bottom. Antimony has become very important, owing to its application in many metallic alloys, such as hard lead and type metal.

Antimony Fluoride. The compound SbF_3 is prepared by dissolving antimony oxide in hydrofluoric acid. This salt readily forms double compounds with alkaline sulphates and chlorides. $(NH_4)_2SO_4 \cdot SbF_3$ is an example of these double salts and is one of the important mordants. The double fluoride of ammonium and antimony, $8SbF_3 \cdot 2NH_4F$, is a useful salt. These compounds make good mordants, and have, to a great extent, replaced tartar emetic.

Argon. This element occurs in the air to the extent of 0.935 per cent. It can be prepared by passing atmospheric nitrogen, free from oxygen and

moisture, over red-hot magnesium ribbon; magnesium nitride is thus formed, whereas the argon does not combine. This element has recently found an extensive application in the argon filled electric lighting bulb, which, on account of its inert nature, is far superior to nitrogen used for the same purpose.

Arsenic. This metal occurs in nature usually in the form of sulphide such as *realgar*, *orpiment*, *smalt*, and *arsenical pyrites*. It is obtained from the pyrites by heating it away from the air, where the arsenic sublimes, leaving the iron sulphide behind.

Arsenious Oxide. White arsenic, As_2O_3, is obtained by roasting arsenical minerals, such as *mispickel*, FeAsS, *cobaltite*, CoAsS, *smaltite*, $CoAs_2$, and other minerals containing arsenic. The roasting is carried on in reverberatory furnaces with free access of air, and the sublimed arsenic trioxide is condensed in suitable chambers. It is purified by resublimation and collected as a white powder. Resublimation under pressure gives a vitreous variety known as *arsenic glass*. It is usually ground to a fine powder, which is slightly soluble in water, and is used principally as an antiseptic for preserving hides; it also finds application in glass manufacture, and its glycerine solution is used in calico printing.

Barium. This element occurs in nature in the form of *heavy spar* or *barytes*, and as *witherite*. It is prepared by heating the oxide with magnesium. It has a metallic appearance with a yellowish tint; but as a metal it has no practical application.

Barium Oxide. This compound can be made by heating the nitrate or hydroxide to a dull red heat. It is manufactured commercially, however, by heating a mixture of barium sulphate and carbon in the electric furnace.

Barium Peroxide. This results when the oxide is heated to 500° C. in the presence of air. At a higher temperature the oxygen is again liberated. It is used in the manufacture of oxygen and hydrogen peroxide.

Barium Hydroxide. This compound is formed when the oxide is treated with water, in which it dissolves, forming a strongly alkaline solution. It is used to some extent in the softening of water; and formerly was an aid in the extraction of sugar from molasses.

Barium Carbonate. Barium carbonate occurs in nature as the mineral *witherite*, and is also prepared by precipitation. It is a good basic material in making other barium compounds.

Barium Chloride. By treating barium carbonate with hydrochloric acid the compound $BaCl_2 \cdot 2H_2O$ is produced. It is used for the manufacture of *blanc-fixe* and in the preparation of certain color lakes.

Barium Sulphate. This compound is found in nature as *barytes* or *heavy spar*. The mineral is ground to a fine powder for use in the manufacture of paints. When artificially made, however, it gives a pigment of finer texture known as *blanc-fixe*. The natural sulphate, when

heated with carbon, is reduced to a sulphide, which, on being dissolved in water and added to a solution of zinc sulphate, becomes the product known as *lithopone*. By treating the barium sulphide with sodium carbonate, the barium is precipitated as barium carbonate, while the sodium is converted into the sulphide. The barium carbonate is filtered off, and the filtrate on evaporation yields crystalline sodium sulphide. This process is of especial value in our country, on account of the large deposits of barytes and the scarcity of witherite.

Bismuth. It occurs in the native state, also as the oxide and sulphide. The ores are smelted in the presence of iron, which acts as a desulphurizing agent. The pure metal has a lustrous appearance like antimony, but may be distinguished from it by a reddish reflex. Bismuth forms easily fusible alloys for making valves, wires, etc., for safety devices on boiler valves, fire doors, and fusible plugs.

Bismuth Nitrate. This is obtained as a crystalline compound containing five molecules of water, when the metal is dissolved in nitric acid and evaporated. It is easily soluble in a small quantity of water, but in a large amount of water it becomes *subnitrate.*

Boron. This element occurs in nature in *boric acid* and *borax.* It is a reduction product, a brown amorphous powder, which, on dissolving in molten aluminium, separates, when cool, in the crystalline form.

Boric Acid. This compound, also known as boracic acid, is found in the steam issuing from fissures in the earth in the vicinity of volcanoes. Boric acid results from the decomposition of borax with hydrochloric acid. It is a colorless, crystalline solid, slightly soluble in cold water, but readily soluble in hot water. It is of value for fusible glazes, for special optical glass, and as an antiseptic and preservative.

Borax. Sodium tetraborate may be prepared by neutralizing boric acid with sodium carbonate. The chief source of borax, however, is from the natural deposits of Thibet and from the crude borax of California, purified by slow recrystallization. A large amount of borax is prepared from the mineral *boronatrocalcite* ($Na_2B_4O_7 \cdot 2CaB_4O_7 \cdot 18H_2O$) by boiling it with soda, or by first converting it into boric acid and then neutralizing with soda. The most common form is the prismatic $Na_2B_4O_7 \cdot 10H_2O$, which on heating effloresces in the air and melts in its water of crystallization, becoming anhydrous at a red heat. Borax is used as a flux in glass and enamel making, in the manufacture of soap, and as a preservative.

Bromine. A description of this element is given in Chapter VIII. It is a good disinfectant, solvent for gold in the presence of platinum and silver, and oxidizing agent.

Cadmium. This element usually accompanies zinc in its ores. It is easily separated as it distills off before the zinc. It does not alter easily when exposed to the air, but becomes covered with a brown oxide when heated. In combination with various metallic alloys it reduces the melting

point. With mercury it forms a soft amalgam which, since it hardens very easily, is a good cement for filling teeth.

Cadmium Sulphide. Hydrogen sulphide passed into a solution of a cadmium salt, gives a bright orange yellow precipitate. This may also be formed by the addition of sodium sulphide. It is known commercially as *cadmium yellow* and is used for tinting paints.

Caesium. This is one of the rare elements and has no commercial value.

Calcium. Very abundant and widely distributed in nature, calcium occurs in the form of carbonate as *marble, chalk,* and *limestone,* in the form of phosphate as *apatite;* of sulphate as *gypsum;* of fluoride as *fluorspar;* of silicate as *wollastonite.* It may be made in the elementary condition by the electrolysis of fused calcium chloride. It has a silvery luster of yellowish tint. Commercially, it is a good agent for removing the last traces of carbon from metals or alloys. It will also reduce some organic compounds.

Calcium Carbonate. Calcium carbonate occurs in many mineral, animal, and vegetable substances. It is decomposed by heat and by mineral or organic acids. It is used in the precipitated form for pharmaceutical preparations, and in the natural form for paints, scouring mixtures, and various other purposes.

Calcium Oxide. By heating calcium carbonate the carbon dioxide is eliminated, and the oxide results. Its method of preparation and its applications are given in Chapter X.

Calcium Hydroxide. This compound forms when water is added to calcium oxide. It is only slightly soluble in water (1.3 parts per thousand) This dilute solution has an alkaline reaction and is known as *lime water.* When an excess of calcium hydroxide is present, it is called *milk of lime.* The milk of lime has many commercial applications, which will be considered at other places in the text.

Calcium Chloride. This compound is a by-product from several industrial operations, especially from the manufacture of soda by the ammonia process, and in the mother liquor from the evaporation of salt brine. It may also be prepared by action upon calcium carbonate with hydrochloric acid. It is very soluble in water. The fused product aids in drying gases; the crystalline product is used in refrigeration for anti-freezing solutions, and for other purposes.

Calcium Sulphate. This compound occurs in nature as *gypsum,* containing two molecules of water of crystallization. When it is heated gently, part of the water is driven off, the resulting product being known as *plaster of Paris.* (See Chapter X.)

Carbon. This element is widely distributed throughout nature in both inorganic and organic substances. In combination with the metals it is found as carbide, also as carbonates like marble and chalk; with hydrogen, it occurs in petroleum and paraffin; with hydrogen and oxygen, in all

vegetable and animal matter; and, with oxygen, as carbon dioxide and carbon monoxide. In the free state it is found as the diamond, graphite, and amorphous carbon.

This element forms thousands of compounds of great commercial value and scientific interest. The study of these compounds constitutes a branch of chemistry called *Organic Chemistry*. Many of these compounds will be considered in other sections of the text, and only two, which are more or less of an inorganic nature, will be taken up at this point.

Carbon Disulphide. This compound is prepared by passing the vapor of sulphur over highly heated charcoal in vertical iron or clay retorts, the sulphur being introduced through a tube on the side. The uncombined sulphur is collected in a special receiver, while the carbon disulphide passes on and is condensed. It is very impure and must be purified by heating first with lead acetate, then with lime water, and finally by redistilling. This compound is also made electrolytically (See Chapter IX). When pure, carbon disulphide is a nearly colorless mobile liquid with only a slight odor. The commercial article, however, has a very disagreeable odor, due to the presence of other sulphur compounds. It is heavier than water, boils at 46.5° C., and its vapor inflames at 149.5° C. It is a good solvent for sulphur, phosphorus, resins, waxes, and fats. It is also used to some extent as a germicide and insecticide.

Carbon Tetrachloride. This compound is made either by passing the vapor of carbon disulphide and dry chlorine through a heated earthenware tube; or by passing chlorine over carbon disulphide in which a little iodine has been dissolved. Sulphur monochloride, formed at the same time, is removed from the carbon tetrachloride with milk of lime and soda, and then distilled. Carbon tetrachloride is a heavy liquid of specific gravity 1.637, and boiling-point 76.5° C. It is a good solvent for gums and resins and is also a constituent of many cleaning solutions. On account of its non-inflammable nature and heavy vapor, it is an efficient fire extinguisher.

Cerium. Derived from the mineral *cerite* this forms both cerous and ceric salts. It is applied in the manufacture of lamp filaments.

Chlorine. This element is discussed in Chapter VIII.

Chromium. Chromium occurs in nature in the mineral *chromite*. It is prepared on a commercial scale by the *Goldschmidt process*, which consists in heating together a mixture of powdered aluminium and chromium oxide. Combined with other metals it hardens them and consequently has found an important place in the manufacture of what is known as *chrome steel*. With nickel it forms an alloy possessing great heat-resisting properties.

Chromium Oxide. This compound results from heating chromium hydroxide, ammonium dichromate, or chromic anhydride. It is useful as a pigment for paint, and for the coloring of glass and enamel.

Chromium Acetate. This comes on the market as a neutral and basic salt. It may be prepared either by the process already described for aluminium acetate, or from sodium dichromate and acetic acid in the presence of a reducing agent. The commercial article is a heavy solution containing about 10 per cent of chromium oxide. Chromium acetate is used as a mordant and for making olive khaki shades.

Chromium Chloride. By passing a current of chlorine over a heated mixture of chromium oxide and charcoal, the chromium chloride sublimes in violet crystals. It is used as a mordant in calico printing and to a limited extent in tanning.

Chromium Sulphate. When chromium hydroxide is dissolved in sulphuric acid, chromium sulphate is formed. It gives a violet or green solution according to the temperature. It is a very good mordant, and, in the basic condition, is used in the manufacture of chrome-tanned leather.

Chrome Alum. The compound $Cr_2(SO_4)_3 \cdot K_2SO_4 \cdot 24H_2O$ is a by-product in many operations where a mixture of potassium dichromate and sulphuric acid acts as an oxidizing agent. It is used as a mordant, and in certain chrome tannages.

Chromic Acid. This compound, also known as *chromic anhydride*, is produced by the action of sulphuric acid on a dichromate. The red lustrous needles are separated from the concentrated solution, dried as rapidly as possible, and preserved in a well-stoppered bottle. The anhydride is a very strong oxidizing agent.

Potassium Dichromate. The material which furnishes the chromium is chrome iron ore or *chromite*. The ore is finely pulverized and mixed with lime and sodium carbonate. A small amount of calcium carbonate is usually added, as the carbon dioxide liberated renders the mass porous. This mixture is heated in a reverberatory furnace in the presence of a strong air current. At the end of the reaction the mass consists of a mixture of calcium chromate, sodium carbonate, and ferric oxide, which, being lixiviated, yields sodium chromate, insoluble calcium carbonate, and ferric oxide. The solution is neutralized with sulphuric acid to precipitate the alumina and silica. It is then filtered and evaporated. When the concentration reaches a specific gravity of 56° Bé., the requisite amount of sulphuric acid is added, converting the chromate to dichromate

$$2Na_2CrO_4 + H_2SO_4 = Na_2SO_4 + Na_2Cr_2O_7 + H_2O.$$

Most of the sodium sulphate separates out by this treatment, and may be collected in the centrifuge. The solution is then concentrated to 60° Bé., when more sodium sulphate separates, and, on standing, the sodium dichromate crystallizes. From this sodium dichromate the potassium salt is obtained by double decomposition. The workmen must avoid breathing the dust or vapor containing chromates, which attack the cartilages of the nose and throat.

The residue of chromium oxide from alizarine manufacture is utilized in preparing dichromate. It is mixed with lime and moulded into bricks, which are subsequently calcined in a current of air. During this treatment calcium chromate is formed, which may be converted into the potassium salt by treatment with potassium carbonate.

Potassium dichromate forms large orange-colored cyrstals, melting at 400° C. and decomposing at a red heat into Cr_2O_3 and K_2CrO_4. It is used in making *chrome yellow* and *Guignet's green*, as a discharge in bleaching oils and fats, in chrome tannage, and as an oxidizing agent.

Sodium Dichromate. The manufacture of this compound has been given above. On account of its cheapness, it has to a large extent replaced potassium dichromate. It is very deliquescent, but if dried at 300° C., it loses water of crystallization and becomes anhydrous, in which conditions it is no longer deliquescent. It is more soluble than the potassium salt and is adapted to the same purposes.

Cobalt. This metal is found in nature as the sulphide. It is obtained electrolytically, and forms both cobaltous and cobaltic salts. In the form of salt, it dries paint oils and as oxide is used in producing colored glass.

Columbium. This occurs in the minteral *columbite*. The oxide forms salts with the alkalies.

Copper. Although found native, this metal usually comes from the minerals *chalcopyrite*, *malachite*, and *azurite*. The ores are roasted to drive off the sulphur or other volatile matter, and the copper oxide remains. The oxide, after reduction in a cupola or puddling furnace with carbon and a siliceous flux is transferred to the converter. The black copper is further refined electrolytically. The electrolytic process gives a very pure product much used in this country. There are many other methods of refining, consisting of wet, dry, and electrolytic processes.

Copper has a bright red, lustrous color. It is fairly hard, but at the same time ductile and flexible. It is easily drawn into wires and finds extensive application in electrical installations, being a good conductor of the current. It is used in the manufacture of cooking utensils and of kettles and evaporators for chemical use. As an alloy metal it is of great practical value, some of the principal alloys which contain it being *brass*, *phosphor-bronze*, *statuary bronze*, *German silver*, *silico-bronze*, and *coins*.

Copper Oxide. This oxide is obtained by heating the metal, the hydroxide, the carbonate, or the nitrate to dull redness. It readily gives up its oxygen to organic matter when heated with it, for which reason it is valuable in organic analysis. Commercially it is a desulphurizing agent in petroleum oils. It is readily soluble in mineral acids, producing salts that have more or less practical application.

Copper Sulphate. This compound is also known as *blue vitriol* and *bluestone*. It is a by-product in the parting of gold and silver by the action of boiling, concentrated sulphuric acid, the silver being dissolved as

sulphate and recovered by precipitating it with metallic copper. Copper sulphate may also be produced by treating scrap copper with a spray of dilute sulphuric acid in the presence of air. Scrap copper mixed with sulphur and heated to a dull red heat yields copper sulphide. This compound, heated in the air, is converted into sulphate and oxide:

$$Cu_2S + O_5 = CuSO_4 + CuO.$$

The copper oxide dissolves in warm sulphuric acid, forming more copper sulphate. The oxidation of some of the natural sulphides of copper yields a mixture of sulphate of copper and sulphate of iron. These sulphates, being isomorphous, cannot be separated by crystallization, but by oxidation of the ferrous to the ferric sulphate, a mixture results which may be separated by crystallization.

Copper sulphate forms blue crystals, soluble in water. Heated to 240° C., it loses its water of crystallization and becomes a white anhydrous powder with a very strong affinity for water. Blue vitriol is used in the preparation of insecticides and germicides, in electrolytic operations, as a mordant, and for many other purposes.

Erbium. This is one of the rare elements and has no practical application.

Fluorine. Fluorine comes from the natural mineral fluorspar. It is a slightly greenish yellow gas, and is one of the most active of the elements, combining directly with hydrogen even in the dark. It attacks all metals except gold and platinum, and immediately decomposes most organic compounds. The element is without practical value at present, although hydrofluoric acid is used for etching on glass.

Gadolinium. This rare element at present has no practical application.

Gallium. Another of the rare elements, is a tough metal that may be cut with a knife. With aluminium it forms a liquid alloy that will decompose water.

Germanium. This rare element belongs to the same group as tin and lead. It has no practical application.

Glucinium. This element is very rare and occurs in the emerald and beryl.

Gold. This precious metal is usually found in the free state and is very widely distributed through the earth's crust. The quantity, however, is so small that it pays to recover it only where the deposit is fairly large. The oldest method of recovering the metal was by levigation, but this was later replaced by the amalgamation process, which consisted in combining the gold with metallic mercury. In recent years, the cyanide process is the most common, and by it even low-grade ores can be worked at a profit. The finely ground ore is treated in tanks with a very dilute solution of sodium or potassium cyanide. The extraction is carried out in a battery, so that the ore may receive several applications, starting with the strongest cyanide solution and ending with water. In this treatment the

compound $2KAu(CN)_2$ is formed. From the cyanide solution the gold is precipitated by adding zinc or aluminium shavings. The sludge is then filter-pressed, dissolved, and purified electrolytically.

Pure gold is a lustrous yellow metal, soft, ductile, and malleable. It is employed in the arts in the form of leaf for gilding, and to a certain extent in chemical technology. For jewelry and coins it is always alloyed with copper. Gold forms both aurous and auric compounds.

Helium. This is one of the rarest of the elements on the earth's surface. It exists in certain uranium minerals and in the air to the extent of 0.0005 per cent. It is absolutely inactive.

Hydrogen. Found free in nature in very small quantities, in combination it is next to oxygen and silicon, the most abundant of the elements, being 11 per cent of the weight of water and a constituent of all organic bodies. When pure, it is a colorless, tasteless, odorless gas. Mixed with air or oxygen and ignited, it combines with explosive effect. In the laboratory it can be produced by the action upon zinc of dilute hydrochloric or sulphuric acid, or by electrolysis and other simple means.

Many methods have been proposed for the commercial production of hydrogen, among which may be mentioned the action of acids on metallic iron, the action of caustic soda upon scrap aluminium, and the separation of the hydrogen formed during the manufacture of water gas. For procuring large quantities, however, the electrolytic processes have met with considerable success. By properly arranged cells the hydrogen is collected at the negative pole, and oxygen at the positive pole. The gas is employed for inflating balloons, for the oxy-hydrogen flame, for the hydrogenation of oils, and in the production of synthetic ammonia.

Hydrogen Peroxide. The action of dilute acids on barium peroxide gives hydrogen peroxide. A mixture of the peroxide and water with the consistency of cream is added slowly to cold dilute phosphoric acid, the temperature of which should not rise over 15° C. The precipitate of barium phosphate is allowed to settle, and the clear liquid decanted. It is best to have the acid in slight excess, as the solution is less liable to decompose.

Peroxides are strong oxidizing agents. Hydrogen peroxide, in which the oxygen is loosely linked, acts as a reducing agent in the presence of certain oxidizing substances. It is used in the bleaching of silk, wool, hair, feathers and ivory. It is a powerful antiseptic, especially in surgery, and prevents processes of fermentation.

Indium. This is one of the rare elements and is of no commercial value.

Iodine. This element is discussed in Chapter VIII.

Iridium. This occurs in very small quantities. It is not dissolved even by aqua regia, and for this reason is used as an alloy with platinum in the manufacture of crucibles that will resist chemical action. The alloy usually contains about 90 per cent of platinum and 10 per cent of iridium. It is also found on the tip of the more expensive gold pens.

Iron. Iron is very abundant in nature and adapted to a multitude of purposes. A full discussion of the metal is given in Chapter XVII. It forms both ferrous and ferric compounds.

Ferrous Acetate. To get this, lead or calcium acetate is added to a solution of ferrous sulphate. An impure product, known as *black iron* or *iron liquor*, is made by adding scrap iron to crude pyroligneous acid. Its principal use is as a mordant in leather dyeing and in calico printing.

Ferrous Sulphate. This compound, also known as *copperas* and *green vitriol*, is a by-product in the manufacture of cement copper. In this process the copper is precipitated from a solution of its sulphate by means of iron. The ferrous sulphide, obtained from the roasting of pyrites in the process of extracting sulphur therefrom, may be allowed to weather in the presence of moisture, by which means both ferrous and ferric sulphates are formed. To the mixed sulphates, scrap iron and sulphuric acid are added, which reduces the iron from the ferric to the ferrous condition. A large amount of ferrous sulphate is obtained from the pickle used in cleaning iron castings.

The solution of ferrous sulphate resulting from the foregoing methods is concentrated by application of heat to the surface of the liquid in such a way as to prevent oxidation. The concentrated solution is allowed to crystallize on wooden rods. The crystals of ferrous sulphate effloresce in the air and become more or less oxidized, basic ferric sulphate being formed. It is soluble in about $1\frac{1}{2}$ parts of water. Ferrous sulphate is most important as a mordant, as a disinfectant, and in the manufacture of ink, Prussian blue, and red oxide.

Ferrous Sulphide. On melting iron and sulphur together a black compound, FeS, results. It is a source for hydrogen sulphide.

Ferric Oxide. This compound occurs in nature in various minerals, or it may be prepared artificially by the rusting of iron. The natural product serves as a source for iron and steel, and in some of its forms is of value as a pigment. The artificial oxide is of various shades, depending upon the method of preparation, and is used almost exclusively in the manufacture of paint.

Ferric Chloride. This compound is obtained by oxidizing ferrous chloride with nitric acid, or by passing chlorine through a solution of ferrous chloride. It is used in the chlorination of copper and silver, and as a mordant in dyeing. Sometimes it is helpful in the purifying of effluent water.

Ferric Sulphate. This may result from the weathering of pyrites in the presence of sulphuric acid. It may also be made by adding sulphuric acid and nitric acid to a solution of ferrous sulphate. Its principal use is as a sewage precipitant.

Ferric Nitrate. By treating scrap iron with an excess of nitric acid (sp.gr. 1.3) and evaporating the solution, colorless crystals are obtained. When ferric hydroxide is added to this solution, a basic nitrate results.

This basic nitrate is used in silk dyeing and weighting, and for coloring buff on cotton. The usual form of " nitrate of iron " consists of basic sulphate of iron and contains oxides of nitrogen.

Krypton. This rare element is present in the atmosphere to the extent of one part in one million. It has a characteristic spectrum and is noticed especially in the *aurora borealis.*

Lanthanum. Lanthanum occurs as a rare oxide in *monazite.* When the oxide is heated, it gives off a very intense white light, which has led to its practical application, together with other rare earths, in the manufacture of gas-light mantles. The mantle made formerly from cotton or linen, is to-day woven from artificial silk. The fabric is dipped into a solution of the nitrate of these rare earths, allowed to dry, dipped again and again, or until a sufficient quantity of the salts has been absorbed, and finally the dry mantle is dipped in a solution of collodion. The mantle is put in position on the burner and the collodion and fiber burnt out, thus leaving a net-work of the oxides, which glow when heated with the characteristic intense light.

Lead. This metal is found abundantly in nature as the mineral *galena,* and to a smaller extent, in various other minerals. There are many methods in vogue for separating the metal, but the one most common in this country is to roast the ore in a reverberatory furnace with a silica flux; the resulting mixture of oxide and silicate is transferred to a cupola furnace where it is heated with coke, lime sometimes being added. The lead thus formed is drawn off from time to time and run into molds, giving what is known as *pig lead.*

Pure lead is bluish-gray, soft, and ductile. Heated in the air, it readily oxidizes. It is not attacked by hydrochloric or sulphuric acids. Nitric, as well as many organic acids, however, dissolve lead very rapidly, forming lead salts, all of which are very poisonous.

Lead is used extensively in chemical technology, especially for building lead chambers and other equipment in the manufacture of sulphuric acid. It is used for making small pipes, small shot, in storage batteries, and as a constituent of many alloys. One of its principal applications is in the manufacture of lead pigments.

Lead Oxide: PbO. On heating metallic lead or residues from the manufacture of *white lead,* a reddish-yellow powder is obtained which is commercially known as *litharge.* This material is important as a drier in paint oils, in the manufacture of rubber goods, and as the raw material for making a large number of lead salts.

Lead Dioxide: PbO_2. This compound, also called *lead peroxide,* comes from treating red lead with nitric acid. It is used extensively in the manufacture of storage batteries, as an oxidizing agent, and in the manufacture of matches.

Minium: Pb_3O_4. Minium, or *red lead,* is prepared either by heating litharge in a reverberatory furnace to a temperature of about 450° C., or

by heating a mixture of litharge and sodium nitrate to a dull red heat. In the form of a paint it makes a good protective coating for steel and iron structures. For machinery and glass manufacture it is also of value.

Lead Carbonate. This material, both neutral and basic, is discussed in Chapter XIII.

Lead Nitrate. By dissolving litharge in dilute nitric acid and evaporating to small volume, colorless crystals of lead nitrate are produced. An excess of litharge gives the basic nitrate.

Lead Sulphate. This compound is made by adding sulphuric acid or a sulphate to a soluble lead salt; also made by roasting sulphide ores. It is discussed in Chapters XIII and XV.

Lithium. Electrolysis of the fused chloride will give lithium. It is a soft metal with silvery luster and specific gravity 0.59, the lightest metal known. The carbonate and salicylate are much used in medicine.

Magnesium. This element occurs in the minerals *magnesite*, *dolomite*, *asbestos*, *talc*, *serpentine*, and in the form of magnesium salts in the Stassfurt deposits as *carnallite*, *kieserite*, and *kainite*. It is prepared in the metallic state by electrolysis of the fused chloride and is of a silvery white color. It is ductile and malleable, and, when heated, may be drawn into wire or ribbon. If heated in a gas flame, it takes fire, and burns to the oxide with a very bright light rich in chemical rays. Two parts of powdered magnesium with one part of potassium chlorate give a very intense light when brought in contact with a spark, hence their extensive use in flashlight photography.

Magnesium Oxide. This oxide is obtained by heating the carbonate to redness. It is common in medicine, and also as a refractory material for furnaces that are required to withstand very high temperatures. It is a part of the Nernst incandescent electric lamp, where it is mixed with the oxides of some of the rare earths.

Magnesium Chloride. The mother liquor of the Stassfurt salts is evaporated to about 42° Bé., when crystals separate consisting of about 80 per cent of $MgCl_2 \cdot 6H_2O$. It makes a good filler for cotton and woolen goods; and is a constituent of magnesia cements. These cements, which are very hard, are known under various trade names, but they nearly all consist of a mixture of magnesium chloride, sawdust, and magnesium oxide.

Magnesium Sulphate. *Epsom salts* is found in many mineral springs, but the most important source is *kieserite* ($MgSO_4 \cdot H_2O$), which is quite insoluble in water, but, on standing in contact with the water for some time, it undergoes solution, becoming $MgSO_4 \cdot 7H_2O$. It is also prepared from *kainite* ($K_2SO_4 \cdot MgSO_4 \cdot MgCl_2 \cdot 6H_2O$); as well as by the action of sulphuric acid on the natural carbonate, *magnesite*. It is a colorless, crystalline salt, readily soluble in water, and efflorescent in dry air. It loses all of its water of crystallization at about 230° C.

Magnesium sulphate has a medicinal value under the name of *Epsom*

salts; it is used in the finishing of cotton fabrics and for weighting paper, silk, and leather.

Manganese. This element does not occur free in nature, but is widely distributed in the form of ores, the principal one being *pyrolusite.* In the metallic condition it is obtained by the Goldschmidt process as a gray lustrous material. In the metallurgy of iron and steel it gives hardness and heat resistance; and has recently been valuable in the making of helmets. Some of its compounds are good oil driers.

Manganese Dioxide. The mineral *pyrolusite* contains this in the natural form. Dissolved in cold hydrochloric acid, it gives the chloride $MnCl_4$, which, when heated, breaks down into the chloride $MnCl_2$ and Cl_2. This reaction is the foundation of the Weldon process for the manufacture of chlorine, described in Chapter VIII. The oxide is used for many purposes, among them the manufacture of oxygen.

Manganous Sulphate. This compound is made by dissolving the carbonate in sulphuric acid. It is used in dyeing and for painting on porcelain.

Potassium Permanganate. This compound is prepared by mixing together potassium hydroxide in solution, manganese dioxide, and potassium chlorate, boiling vigorously, and evaporating to a paste. The paste is then heated in a crucible to a point of fusion, dissolved when cold in water, and oxidized with chlorine or ozone. The permanganate crystallizes from the concentrated solution in metallic looking crystals. It is fairly soluble in water, giving a purple color. It is a strong oxidizing agent for organic and inorganic substances; it bleaches vegetable fibers and purifies various gases. Recently sodium permanganate has largely replaced the potassium salt.

Mercury. This is the only metal that is liquid at ordinary temperatures. Existing to a slight extent in the free condition, it comes almost exclusively from *cinnabar.* From this mineral, which is the sulphide HgS, it is prepared by distilling in a free supply of air. The mercury distills over and is condensed, while the sulphur burns to sulphur dioxide.

Mercury is a silvery white liquid with specific gravity 13.6. It combines with nearly all of the metals, except iron, forming amalgams of varied practical applications. The mercury-vapor electric lamp of Bastian consists of a long, horizontal tube containing a small quantity of mercury. At each end of the tube, which is under high vacuum, is an electrode. By passing a current through the mercury it becomes vaporized; and the vapor, acting as a conductor, gives off a very intense light. The largest amount of mercury is required for the extraction of gold and silver, but considerable is also necessary for chemical and physical apparatus. Mercury forms both mercurous and mercuric compounds.

Mercuric Oxide. This oxide is produced by heating mercuric nitrate and mercury in an iron crucible. Bright red in color, it is sometimes known as *red precipitate.*

Mercurous Chloride. This compound, also called *calomel*, is prepared by heating a mixture of 4 parts of mercuric chloride with 3 parts of metallic mercury. It is heated in an iron pot until a white mass forms. The temperature is then raised, and the mercurous chloride sublimes. It is then further purified by washing.

Mercuric Chloride. Another chloride, also known as *corrosive sublimate*, is made by subliming a mixture of mercuric sulphate and sodium chloride in the presence of a small quantity of manganese dioxide, also by dissolving mercuric oxide in hydrochloric acid. Commercially, however, it is made by heating mercury in the presence of chlorine gas. Being a violent poison, it should be handled with great care. In very dilute solutions it is an effective antiseptic for medicinal purposes; on an industrial scale, it is used for impregnating timber.

Molybdenum. The mineral *molybdenite* gives the oxide MoO_3 when roasted. The metal is derived from the oxide heated with carbon in a stream of hydrogen in the electric furnace. It is a gray powder, which, on fusing, becomes silvery in appearance. The metal is used in manufacturing some of the hard steels; and the oxide is the source of molybdates.

Neodymium. This is one of the rare earths and has no practical application.

Neon. This is another of the rare elements of the atmosphere.

Nickel. This metal contained principally in *garnierite*, $2(NiMg)Si_4O_{12} \cdot 2H_2O$, is extracted by heating the mineral with coke and a basic flux, subsequently puddling in an open-hearth furnace with hot air to separate the iron, manganese, and silicon. The crude nickel resulting from this or other methods constitutes what is known as *nickel matte* and is purified by electrolytic means.

Pure nickel has a silvery appearance, is ductile, and slightly magnetic. It remains unchanged in the air and consequently is a part of many alloys, such as *nickel coins* and *German silver*. It is also much used for electroplating iron, for making nickel-steel and armor-plate, and in the manufacture of various utensils. In the finely divided condition it is a good catalytic agent. Combined with chromium it forms an alloy having a very high resistance, and found largely in electrical heating apparatus.

Nickel Sulphate. Nickel dissolved in sulphuric acid form bright emerald green crystals of nickel sulphate. It is important as an electrolyte in electroplating.

Nitrogen. In the free state, nitrogen forms about four-fifths of the atmosphere. It is also abundant in ammonia salts, nitrates, and many organic substances. Heating a mixture of potassium dichromate and ammonium chloride will give pure nitrogen. Many commercial methods have been proposed. The liquid air method, however, seems to be the most satisfactory. Formerly, nitrogen was thought to be one of the most inert of the elements; at present, however, this idea has been greatly

modified, as we now have many compounds formed by direct union with the element.

Some nitrogen compounds are a very vital factor in the production of crops. As the natural supply of nitrates and ammonia is becoming limited, we have had to devise ways and means for separating this much-needed element from its inexhaustible source, the atmosphere. (See Chapter IX.)

Osmium. One of the rare elements, this has the highest specific gravity (22.48) of any of the metals; it also has the highest melting-point, and in the mass is not affected even by aqua regia. From the fact that its oxide OsO_4 produces a highly poisonous and irritating vapor, it has been suggested as a trench gas in modern warfare.

Oxygen. Oxygen is the most abundant and important of the elements, being found in the air to the extent by weight of 23 per cent, in water, 89 per cent, as well as in minerals, acids, salts, and animal and vegetable matter. It combines either directly or indirectly with all elements except fluorine, helium, and argon. It is a colorless, odorless gas. In the laboratory it may be prepared in various ways. Many industrial methods of preparation have also been proposed, but of these only a few have proven of practical and economic value.

Electrolytic Oxygen. Among the processes recently devised is that based upon the electrolysis of water in specially arranged cells. This, it is claimed, has many advantages over the others, especially as hydrogen is generated at the same time. The equipment, however, is somewhat expensive and depends largely upon the cost of electrical power. It can, of course, be operated to greater advantage where electrical energy is readily available.

Boussingault-Brin Bros.' Process. In the original process barium oxide is heated to a dull redness in a current of air, freed from carbon dioxide. At this temperature it absorbs oxygen and becomes barium peroxide. After the reaction is complete, the heat is raised to bright redness, whereupon the barium peroxide is dissociated into barium oxide and oxygen. The process would be continuous and the barium oxide could be used repeatedly, if it did not become glassy and hydrated. Inasmuch as the reaction cannot be repeated successfully more than ten or twelve times, the process is not practical. Gondolo proposed the intimate mixing of lime of magnesia with the barium oxide. This prevents, to a certain extent, the production of hydrate, so that the operation may be repeated 125 times.

The modification introduced by the Brin Brothers consists in heating the barium oxide to a dull redness in retorts into which pure air is forced under a pressure of about 15 pounds to the square inch. When the barium oxide has been converted to the peroxide, the pressure pump is reversed and a vacuum of about 27 inches produced, the temperature remaining the same. Under these conditions one atom of oxygen is evolved from the

barium peroxide. The operation is a continuous one, except that the barium oxide must be revivified every six months.

Thessie du Motay-Marechal Process. In this process a mixture of manganese dioxide and caustic soda is heated in a current of dry air to dull redness, sodium manganate being formed. The properly granulated mass is now heated to 450° C. in a current of steam, when the following reaction takes place:

$$Na_2MnO_4+H_2O=2NaOH+MnO_2+O.$$

To secure regularity in the reaction, a small amount of cuprous oxide may be added to the mixture. As manganese dioxide and sodium hydroxide are regenerated in the second reaction, the process in a continuous one.

Oxygen from Liquid Air. Liquid air machines have been perfected so that their operation has become very economical. If liquid air is allowed to evaporate, the nitrogen passes off more readily than the oxygen. By use of double-walled vacuum vessels, the evaporation takes place so slowly that most of the nitrogen escapes, leaving fairly pure oxygen. By this method the oxygen gas contains about 10 per cent of nitrogen.

Oxygen is used in the oxy-hydrogen blow pipe, in the manufacture of blown oils, in the aging of liquors, in glass refining, in medicine, and in the oxy-acetylene welding process.

Ozone. This peculiar form of oxygen was first observed by Van Marum in 1785, who passed a current of air through an electric discharge. It is a colorless gas of chlorine-like odor. Under great pressure its color is blue, and when liquefied it becomes dark blue, mobile, and highly magnetic. The chemical formula is O_3; and the molecular weight is 48. At ordinary temperatures it is relatively stable, but decomposes in contact with organic or in general, oxidizable matter, and spontaneously at 260° C. Ozone may be formed in various ways, viz.: by chemical action, by electrolysis, by the electrostatic field, by ultra-violet rays, by radio-active elements, by incandescent solids, and by vaporization of water. Of the chemical methods, the heating of peroxides or potassium permanganate with strong sulphuric acid may be mentioned; but the production by the electrostatic field has been the only one developed commercially, although the theory of the latter is not fully understood, it is probable that ionization by collision takes place with consequent dissociation of the oxygen, which, on recombination, furnishes aggregates of ions consisting of molecules with an attached extra atom.

Machines. Ozone generators are of various types. The essential principle of all is the juxtaposition of two, or a plurality of, discharging surfaces so as to form a condenser with an air gap which may or may not be furnished with a dielectric element. The discharging surfaces may be smooth or armed with points, and, if smooth, they may be flat or curved. Ozonators without dielectrics generally possess rotating electrodes so that they are in relative motion with the aim of averting sparking, which favors

the formation of nitrogen oxides and the destruction of ozone already formed.

The great majority of successful ozone generators have smooth electrodes and dielectrics, and are divisible into two types: the cylindrical and the plate. In a typical form of plate ozonator two outer plates are pierced at the center and the ozonized air is aspirated through tubes inserted in the holes. The air enters at the peripheries of the plates and passes through the field to the center. Cooling is effected by means of flat rectangular water boxes in contact with and between the two inner plates. The two outer boxes are earthed and form the ground side of the circuit; the inner box is insulated and constitutes the high potential element of the ozonator. The boxes are all furnished with circulating water that in the inner, high-tension box being introduced and removed by having the water fall through the air a distance sufficient to insure against waste-

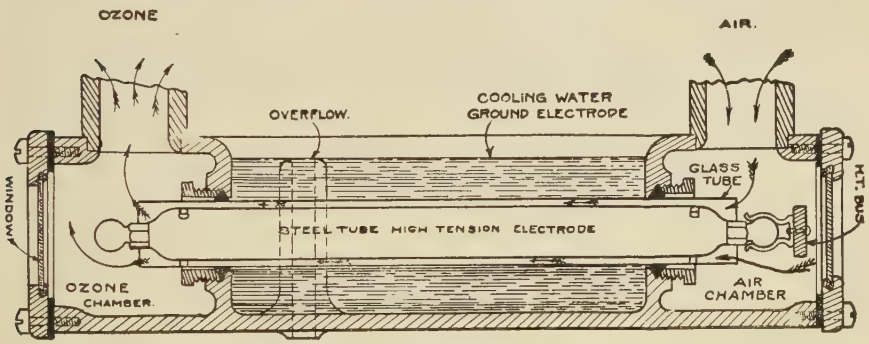

FIG. 119.

ful current leakage. The whole structure is commonly enclosed in a glass retaining case into which suitable dry air is introduced. The advantage of this type of ozonator is that as the field is produced between the two glass plates, the labor necessary to keep the machine clean is nominal. The disadvantages are difficulty of disassembling and assembling, high potential required, complexity of the cooling system, large space occupied and danger of shut down of the whole system through failure of one unit.

A representative tubular unit is shown in Fig. 119. This consists of a cast-iron frame with two closed bulkheads connected by the ozone tubes in much the same way as in a water-tube boiler. Within these tubes, which are of glass, the cylindrical, high-tension electrodes are placed coaxially. The outer tubes are immersed in water, which furnishes the ground element, while the inner, high-tension elements are connected to the circuit by means of suitable contacts on a bus bar, carried into the air header through insulating bushings. The air is introduced into the rear header

and passes through the tubes to the front, whence it passes into the ozone collecting pipe. This machine requires cleaning out from time to time, but the operation is simple and quickly performed. The door of the ozone header is removed, the inner electrodes drawn out, and the tubes cleaned with a swab.

Commercial ozonators are commonly operated on voltages ranging from 5000 to 20,000, and at frequencies of from 50 to 500 cycles per second. A transformer is used to generate the current. Special high frequency generators are usually furnished in all but the smallest installations, for the capacity of an ozone generator is almost proportional to the frequency employed, and the use of 500-cycle currents results in multiplying the capacity of a given generator by ten as compared with operating it on 50 cycles.

An essential to successful and economical operation is dry, dense, and cold air, consequently most installations, excepting very small ones, include a means for refrigerating the air. It has been found in practice that air cooled to about zero centigrade possesses the requisite dryness, and that further cooling is uneconomical, because, although the efficiency yield of the ozonator is increased, this is only at the expense of relatively greater cost for refrigeration.

Concentrations and Yields. For most industrial purposes the concentration should be in the neighborhood of from two to three grams per cubic meter of air, although in some special cases it may be as high as five grams. It is rarely found expedient to operate at greater concentrations. The average yield is about fifty grams per kilowatt hour, and, although much higher yields are claimed from time to time for certain types of generators, there are none in commercial operation. It is also significant that drawing the ozone through an acidified solution of potassium iodide, a procedure which is often followed in analysis, gives an incorrect result which may be from 50 to 60 per cent higher than the correct value.

Applications. The applications of ozone are dependent upon the fact that it is a powerful oxidizing agent and that it oxidizes most substances at temperatures much below those at which they are capable of combining with ordinary oxygen.

Ventilation. Ozone is used in ventilation chiefly, because of its power to destroy organic odors. It has been shown that it is capable of oxidizing the odors arising from various animal and industrial activities: e.g., those of valerianic acid, butyric acid, skatol, indol, decayed foods, fish, tanners' scrap, manure, etc. The causes of distress in vitiated air are heat, moisture, and crowd odors. It is not believed that the organic excreta causing the latter are poisonous, but it is generally conceded that the odors constitute a real cause of objectionableness in stale air. Prof. Bass has recently conducted experiments on school children, which have established the fact that the addition of about 1 part of ozone in a million parts of air

determines the difference between tolerable and intolerable conditions, when the air supply is very small.

It was at one time supposed that on account of the very great bactericidal power of ozone it would prove valuable in disinfecting the air of dwellings and factories, but it has been shown that in breathable concentrations it has little effect on the dry bacteria in the air. This, however, is immaterial, as it is now generally accepted that the dried bacteria in the air are not concerned in its vitiation nor in disease transmission. In suitable concentrations ozone may be used for disinfecting and deodorizing rooms that have become contaminated or infected.

Water Purification. The purification of potable water constitutes one of the most important applications of ozone up to the present time. The advantages of the method are the non-poisonous nature of the reagent, the insolubility that insures against an excess remaining in the water, and the fact that, besides rendering the water sterile, it removes all taste and odor due to organic defilement.

Water to be ozonized ordinarily requires rough filtering to remove the bulk of the organic matter, about 97 per cent being thus eliminated. The ozone is relied upon to destroy the bacteria, smell, taste, and color persisting after filtering. The ozone is introduced into the water under pressure and intimately mixed with it by suitable mechanical means, such as agitation or forcing it through the interstices between broken rock or the like, or through sieves.

Technical. The technical applications of ozone are very numerous and are increasing daily in number. Oils, fats, tallows, and waxes may be bleached, deodorized, rendered tasteless, and otherwise purified by means of ozone.

Raw linseed oil may be converted into a good drying varnish by having ozone blown through it. At ordinary temperatures this bleaches the oil and increases its viscosity. At elevated temperatures the oil darkens, and it may be so completely dried as to be useful for the manufacture of linoleum. Raw menhaden oil may be clarified, deodorized, bleached, and greatly thickened in the same manner. Raw cotton-seed oil is bleached and deodorized, besides being rendered viscous.

Ozone is applied to bleaching cotton, linen, and silk fabrics. It possesses great advantages over chlorine in that it is non-poisonous and does not have to be mixed in vats which suffuse the buildings with fumes.

Ozone is used successfully for drying oil varnishes, as in the manufacture of patent leather. If it is mixed with varnish, the latter dries quickly and evenly throughout its thickness; and if varnished surfaces are exposed to ozone, it causes the formation of a protective surface while the underlying layers harden more slowly.

Ozone is important to the cold-storage industry. For many substances there exists a critical temperature below which they may not be stored

without danger or damage, and above which bacterial proliferation and other putrefactive causes result in deterioration. It is difficult to maintain these critical temperatures in rooms the doors of which are being opened and shut constantly, and it has been found that with the aid of ozone all deleterious processes may be suppressed, even though the temperature rises several degrees above the critical point.

In the brewery, ozone is becoming widely used for sterilizing and drying the casks and in providing water of unsurpassable quality for brewing. Recent researches have shown that it increases the power and activity of yeast.

Alkaline Peroxides. By heating 100 parts of alkali with 70 to 90 parts of lime or magnesia to a temperature of bright redness, an alkaline oxide is formed. The alkaline oxide, heated in a current of dry air at a temperature of about 500° C., is converted into the peroxide. The pulverized mass is slowly added to water and, after the elimination of the lime or magnesia, yields an effective bleaching solution. By the addition of soluble salts of calcium, barium, or strontium to this solution, the peroxides of the alkaline earths are precipitated. The alkaline peroxides may also be prepared by exposing the fused metal at a temperature of 300° C. to a current of purified, dry air.

Palladium. This rare element exists to a limited extent in combination with gold. In the spongy condition it absorbs hydrogen with rapidity, and marked increase in temperature. Advantage is taken of this fact in making automatic gas lighters. Palladium, alloyed with gold, is a white lustrous body being used quite extensively as a substitute for platinum in jewelry and dentistry, and for many other purposes.

Phosphorus. Tribasic calcium phosphate, $Ca_3(PO_4)_2$, in the form of bone, bone ash, and mineral phosphate is a source of phosphorus. The finely ground material is treated with sulphuric acid (sp.gr. 1.52) in lead-lined tanks. This converts the tricalcium phosphate into monocalcium phosphate. The clear solution is drawn off, and the precipitate thoroughly washed with hot water. The solution and washings are evaporated in leaden pans to 45° Bé., about 25 per cent of coke or charcoal added, and the pasty mass dried in iron pans. The dry mixture is then subjected to distillation in fireclay retorts, usually placed in two tiers. At the start of the operation the monocalcium phosphate is changed to the metaphosphate, which, in the presence of carbon, forms tricalcium phosphate, phosphorus, and carbon monoxide. The neck of the retort is passed into a condenser containing water, under which the phosphorus collects. By this method about two-thirds of the phosphorus in the phosphate is set free.

Electrical processes are taking the place of the older methods for the manufacture of phosphorus. A change of the mineral phosphate, coke, and sand is heated in an electric furnace and gives a yield of about 86 per cent.

The crude phosphorus is purified by filtration through porous tile, chamois skin, or canvas, under warm water, which keeps the phosphorus liquid. It may also be purified by melting under a warm solution of potassium dichromate and sulphuric acid. Its final purification is by redistillation in iron retorts.

Ordinary phosphorus, a yellow, wax-like solid, melts at 44° C., has a specific gravity of 1.82, and distills at 269° C. It appears on the market in the form of sticks, which, being highly inflammable, must be kept under water.

Red Phosphorus. The amorphous form is prepared by heating ordinary phosphorus in closed iron pots to a temperature of 250° C. for several days. There always remains some unchanged phosphorus which must be removed by treating the mass with boiling caustic soda or carbon disulphide. It is a reddish-brown substance, which only inflames in the air when heated to about 260° C. It is insoluble in water and carbon disulphide, and, unlike ordinary phosphorus, is not poisonous.

Yellow phosphorus is used in making matches and phosphor bronze; the red variety is one of the constituents of safety matches.

Phosphoric Acid. This acid is prepared from bone ash or mineral phosphate by the action of sulphuric acid. The filtered solution is concentrated to a syrupy consistency, which contains about 85 per cent of H_3PO_4. If further heated, it loses one molecule of water and becomes metaphosphoric acid, called *glacial* phosphoric acid.

Platinum. This metal occurs naturally as small granules in the sandy deposits of the Ural Mountains, from which it is separated by levigation. It is mixed with some of the other rare metals, which can be eliminated by treatment with aqua regia and subsequent precipitation. Pure platinum has a silvery appearance, is one of the noble metals, and is not altered in the air even at elevated temperatures. It alloys with other metals, and is affected by fused alkaline hydroxides, phosphorus, cyanides, sulphides, and halogens. It is a part of many forms of chemical apparatus and is being adopted extensively in the manufacture of jewelry. It is most important commercially as a catalytic agent in the production of contact sulphuric acid and in the conversion of ammonia into nitric acid.

Potassium. This element is abundant in nature in combination with various other substances. It is present in all soils and is essential to vegetable life. The principal source is from *feldspar* and the Stassfurt deposits. For many years Germany had controlled the market of the world for this metal and its compounds. Since the outbreak of the European war many methods have been proposed for obtaining these compounds from other sources, as it has become especially imperative for this country to be independent of Germany for its supply. Among the methods giving the most promise and already yielding large quantities of potash may be mentioned the recovery from the brine of Searles Lake, California; from kelp; from feldspar; from cement factory dust; and its recovery in the

residue from many organic materials. The production of potash in America in 1915 was 350 tons; in 1916 it had increased to 35,739 tons; while, for 1918, the figures indicate a phenomenal output. The preparation of the element is similar to that given later under sodium, and like sodium it forms an extensive series of valuable compounds.

Potassium Carbonate. This compound, also known as *potash* and *salts of tartar*, is found in the ashes of wood and plants, beet sugar residues, and wool scourings, but the largest quantity is derived from the chloride by the same methods as for the corresponding sodium salt. The use of potassium carbonate is somewhat limited.

Potassium Hydroxide. *Caustic potash*, the common name for the hydroxide, is made by adding milk of lime to a solution of carbonate. The industrial method common at the present time, however, is the same as that employed for sodium hydroxide. The principal use of this alkali is in soft and liquid soaps.

Potassium Chloride. This compound is separated by crystallization from its abundant source, the Stassfurt deposits, which have furnished the chief raw material for all potassium compounds.

Potassium Nitrate. Known and used for hundreds of years, the nitrate is found in nature, to a limited extent, but is mostly prepared from sodium nitrate by double decomposition with potassium chloride. Its principal use is in the manufacture of black gunpowder and fertilizers.

Potassium Ferrocyanide. The oldest method of manufacture consists in heating scrap iron with a mixture of organic compounds containing nitrogen, such as horns, hoofs, hides, dried blood, and potassium carbonates. The modern method is to fuse potassium carbonate in iron crucibles and add in small portions the nitrogenous material. The action is very violent and must be conducted with care. After the reaction is complete, the fused mass is lixiviated to separate the ferrocyanide from the carbonaceous matter. The solution is evaporated to a sp.gr. of 1.27, wherefore the ferrocyanide crystallizes out. As the first product is very crude, it must be subjected to recrystallization.

Potassium Ferricyanide. This is prepared by action upon the ferrocyanide with a current of chlorine:

$$K_4Fe(CN)_6 + Cl = KCl + K_3Fe(CN)_6.$$

Potassium Cyanide. By fusing potassium ferrocyanide with potassium carbonate a change takes place resulting in the formation of potassium cyanide and potassium cyanate, the latter being mostly eliminated by the addition of carbon during the reaction.

Praseodymium. This rare element occurs together with the other rare earths, in the *monazite* sands.

Radium. For many years fluorescence and phosphorescence have been known. Some substances give off light after being exposed to sunlight, but

eventually lose the property when kept for some time in a dark place. Phosphorescence, as we have long known, may result from friction or other causes. Recently, however, some very interesting substances have been discovered which emit heat and light without external stimulation. These "*radio-active*" substances have been much studied during the past few years, and the discoveries made have marked a wonderful era in the development of both chemical and physical science. Becquerel in 1896 discovered that *uraninite*, or *pitch-blende*, emitted radiations capable of affecting a photographic plate by rays that could neither be reflected nor refracted. These rays, it was also learned, rendered gases good conductors of electricity and converted insulating materials into conductors of the current. Becquerel attributed these properties to uranium and its compounds, but in 1898–1899 Madame Curie and her husband, Professor Curie, demonstrated that the emanations were more marked in the residues from pitch-blende that uranium had been removed from. By using enormous quantities of the residues they were eventually able to separate a substance a million times more active than uranium, and to this they at first gave the name of *polonium*, but afterwards called it *radium*. This original radium of the Curies has since been shown to contain other elements, but it is not within the scope of this chapter to deal with all of the interesting features that have developed from this wonderful discovery.

Radium is an element somewhat similar to barium in its chemical properties; it forms salts with the mineral and organic acids. One very interesting point is that radium is supposed to be a metal in the stage of decomposition, for the emanations given off have been condensed and proven to be the element *helium*.

Rhodium. This is one of the rare elements belonging to the platinum group. It is a silvery white metal, insoluble even in aqua regia. It is used in the construction of electrical pyrometers.

Rubidium. This is one of the rare elements and occurs in lithium-bearing minerals. Its properties are somewhat similar to potassium.

Ruthenium. This belongs to the platinum group of rare elements and has properties somewhat similar to that metal.

Samarium. *Monazite* contains this but it has no commercial applications.

Scandium. This belongs to the same group as samarium and is of no commercial importance.

Selenium. This element occurs in some of the Bohemian and Swiss pyrites and is found in the dust chambers and in the mud of the lead chambers of sulphuric acid works. The selenium is recovered by treating the dust and mud with a concentrated solution of potassium cyanide and reprecipitating with hydrochloric acid. The crude selenium is oxidized with nitric acid to SeO_2, and then purified by sublimation. The metal may be obtained by reducing with sulphur dioxide.

Heated in the air, selenium burns to the oxide, giving off an odor of rotten onions. The metal may be in an amorphous or crystalline condition, the latter form being a good conductor of electricity, the conductivity increasing with the illumination. On account of this property, it finds application in wireless telegraphy and in the wireless telephone. Much research work has been conducted along applied lines, but up to the present time there are many difficulties still unsolved. The salts, proposed as a treatment in some of the so-called incurable diseases, have met with a certain amount of success.

Silicon. This element does not occur in the free state, but in combination as silicon dioxide and silicates it constitutes the bulk of the earth's crust. In the free condition it may be prepared in various ways, one being the heating of powdered silica with powdered metallic magnesium. By modern processes of heat treatment in the electric furnace, silica is fused to a transparent glass from which is made chemical apparatus both for laboratory and industrial purposes.

Water Glass. Soluble glass or water glass consists of soluble silicates of sodium or potassium, or a mixture of the two. It usually comes on the market as a thick, syrupy liquid. In its manufacture a mixture of sand, charcoal, and soda is heated together in a reverberatory furnace for eight to ten hours. The glass-like mass is broken up and boiled with water. The resulting solution is filtered and concentrated to the proper consistency.

Water glass is used to render tissues non-inflammable, to protect wood and porous stone, to adulterate cheap soaps, to fix pigments on calico and colors on mural paintings, to make artificial stone, and also to cement glass and pottery.

Silver. This metal is found free in nature and in combination with other elements, principally as the sulphide. Lead, when used with the proper flux, has the power of withdrawing silver from its ores. The lead buckle is heated in a furnace with an excess of air whereupon the lead burns off, leaving the silver behind. Silver is found in the sludge from the electrolytic deposit of copper, and is a by-product in other metallurgical operations. Many other methods have been proposed. Pure silver has a white, lustrous color. It is the best known conductor of electricity. It does not oxidize when exposed to the air, even if heated, and so is classed as one of the noble metals. It is a constituent of many alloys for jewelry and coins. Large quantities are also consumed for silver plating.

Silver Chloride. This compound is found ready formed in nature as the mineral *horn silver*, or it may be prepared by adding sodium chloride to a soluble silver salt. Although insoluble in water, it dissolves easily in ammonia, potassium cyanide, and sodium thiosulphate. It is required extensively in the preparation of photographic papers.

Silver Bromide. By adding sodium bromide to silver nitrate this com-

pound is formed. It is applied in making the photographic dry plate and in gaslight papers.

Silver Iodide. When sodium or cadmium iodide is added to silver nitrate, silver iodide results. It is applied in the manufacture of photographic dry plates and developing papers.

Silver Nitrate. By dissolving pure silver in dilute nitric acid silver nitrate is obtained. If a copper-silver alloy is used, the copper may be eliminated by evaporating to dryness and heating the dry mass to a temperature of 250° C. The copper nitrate is decomposed, yielding copper oxide, and as the silver nitrate is not affected, it may be dissolved in water and the solution evaporated to crystallization. It is a colorless salt, soluble in water, melts at 225° C., and decomposes at dull red heat. It is used in photography, in the preparation of indelible ink, as a cautery, and for silvering the back of mirrors.

Sodium. This metal is not found in the free condition in nature but is widely distributed in combination with other substances, and is especially abundant as the chloride or common salt. It may be procured in various ways, and the commercial methods are given in Chapter IX.

Metallic sodium has a silvery appearance closely resembling potassium. It is oxidized rapidly when exposed to the air, and so must be preserved under petroleum. Sodium as a metal has only a very limited application, although formerly it was used to quite an extent in the preparation of metallic aluminium.

Sodium Peroxide. This compound is prepared by heating sodium to 300° C. in aluminium pans in a current of dry air. It is a very energetic oxidizing agent at elevated temperatures, and, when dissolved in water, gives off atomic oxygen, thus rendering it of value as a bleaching agent.

Caustic Soda. This product is made by causticizing sodium carbonate with lime. The purified tank liquor, which must be kept at a specific gravity of 1.1, is treated with lime at a boiling temperature. Water or dilute liquor must be added to avoid reverse action. In the Thomas process the reaction may be carried out in a concentrated liquor under pressure and at a temperature between 140° to 145° C. The calcium carbonate is allowed to settle, and the supernatant liquor filtered through sand and carbon. The solution of caustic soda is evaporated in cast-iron kettles until all of the water is driven off and the alkali remains as a fused mass. The lower compounds of sulphur, such as thiosulphate, may be oxidized by the addition of a small quantity of sodium nitrate. For transportation, the fused caustic is run into sheet-iron drums, which are closed as soon as cold to prevent absorption of water and carbon dioxide.

Caustic soda may be purified by solution in pure alcohol, which dissolves the hydroxide, but not the carbonate. A still purer form results from the action of metallic sodium on distilled water.

There are a number of electrolytic processes for the manufacture of caustic soda, discussed in Chapter VIII.

Sodium hydroxide is used in large quantities in the manufacture of soap, in the manufacture of paper pulp, for mercerization of cotton, in the manufacture of dyestuffs, in the purification of mineral oils, and for various other purposes.

Sodium Carbonate. Before 1791, sodium carbonate was found in natural deposits and the ashes of marine plants. At the time of the French Revolution, Leblanc brought forward his method for the commercial production of soda from salt. The process, introduced in 1791, held sway without competition until 1863, when the Solvay process (ammonia-soda) made its appearance. This would probably have entirely replaced the Leblanc process were it not for the valuable by-product, hydrochloric acid, formed during the operation of the latter. At present the Leblanc process furnishes a little less than half of the sodium carbonate consumed.

Leblanc Process. The action of sulphuric acid on common salt gives sodium sulphate. The sodium sulphate is then transformed into carbonate by the action of carbon and calcium carbonate, the reactions involved being represented by the following equation:

$$2NaCl+H_2SO_4=Na_2SO_4+2HCl,$$

$$Na_2SO_4+2C=Na_2S+2CO_2,$$

$$Na_2S+CaCO_3=Na_2CO_3+CaS.$$

Preparation of Sodium Sulphate or Salt Cake. The reaction takes place in two stages, viz.:

$$NaCl+H_2SO_4=NaHSO_4+HCl,$$

$$NaCl+NaHSO_4=Na_2SO_4+HCl.$$

The furnace used for this purpose is described elsewhere. The first reaction takes place at a comparatively low temperature and at the back of the furnace. When it slackens, the charge is raked forward and is exposed to a higher heat, whereupon the second reaction takes place. The sulphuric acid should be between 57° and 60° Bé. Below 56° Bé. it would attack the cast-iron pan of the furnace, and above 60° Bé. it forms lumps of salt with an anhydrous coating of sodium sulphate. This coating prevents the penetration of the acid, thus making the action irregular and incomplete.

Conversion of Salt Cake into Carbonate. The salt cake should contain no sodium chloride and but little free sulphuric acid. It should be porous and friable, for which purpose it is exposed to the action of the air for two or three days. It is now mixed with limestone and powdered coal, the proportions indicated by Leblanc being:

Sodium sulphate	100 parts
Calcium carbonate	100 parts
Carbon	50 parts

Common practice is to use an excess of limestone and coal. At the end of the operation, when the temperature has reached about 1000° C., the calcium carbonate in excess is decomposed with the formation of lime and carbon dioxide. The latter, coming in contact with the carbon, is converted into carbon monoxide. The blue flame which appears indicates that the reaction is complete. The passage of the carbon monoxide through the mass renders it porous. The limestone should be very pure, as silica and aluminium would cause the formation of silicates and aluminates. The coal should contain little or no nitrogen, because this gives rise to cyanides, which react upon iron to form ferrocyanides and, in small quantities, cyanates.

Black Ash. In the manufacture of black ash, the mixture of sulphate, carbon, and limestone is introduced into the back of a black ash or balling furnace, which is a long reverberatory furnace. The mixture is heated at a rather low temperature at first; then, after some time, the charge is raked forward nearer the grate where the temperature is much higher, reaching 1000° C. The mass is stirred until it stiffens and the blue flame appears, indicating the end of the reaction. It is now worked together into a ball and raked into wagons, where it rapidly solidifies. On exposure to the air for two or three days, the small quantity of lime present slakes, rendering the mass friable and easier to lixiviate. The hand-worked furnace is being replaced by the revolving furnace, as shown in Fig. 27.

Good black ash is of a very dark brown or gray color with porous fracture. It contains about 45 per cent of sodium carbonate, 30 per cent of calcium sulphide, 10 per cent of calcium oxide, 6 per cent of calcium carbonate, and small amounts of sodium silicate, sodium aluminate, sodium sulphide, sodium chloride, ferric oxide, and coal, while very slight amounts of cyanide, ferrocyanide, and thiosulphate are usually present.

Lixiviation of Black Ash. When properly made, black ash is easily extracted by Shank's process. The material is placed in tanks having false bottoms and is systematically treated with water. The fresh water comes in contact with the nearly exhaused ash, and, as it becomes more concentrated meets the fresh ash. The lixiviation should be done at the lowest possible temperature, and the ash kept covered with water to avoid contact with the air. Where these precautions are not observed, secondary reactions take place, which reduce the yield of sodium carbonate.

Purification and Evaporation of Tank Liquors. The principal impurities of tank liquor are caustic soda, sodium sulphide, sodium thiosulphate, sodium ferrocyanide, sodium ferro-sulphide, and traces of other compounds. The liquor is allowed to clarify by sedimentation and is then

passed through carbonating towers, where it trickles over porous substances and comes in contact with a current of carbon dioxide and air. The caustic soda and sodium sulphide are here converted into carbonate, the ferro-sulphide is decomposed, and any iron, silica, and aluminium present are precipitated.

Paulie's Process. In this process MnO_2, as Weldon mud, is added to the liquor, and superheated steam and air passed through it. Sodium sulphide is oxidized to sulphate, and any iron, silica, and aluminium are precipitated.

In either case the purified liquor is evaporated in cast-iron pans. As it becomes concentrated, a crystalline powder separates, $Na_2CO_3 \cdot H_2O$, which by calcination at a red heat is converted to Na_2CO_3. The mother liquor (red liquor) is further purified or used for the production of caustic soda. This red liquor usually contains a large amount of caustic soda and sodium sulphide.

Instead of calcining the $Na_2CO_3 \cdot H_2O$, it may be converted into soda crystals (sal soda) by dissolving in hot water and allowing it to crystallize slowly. In this way large, nearly pure crystals of $Na_2CO_3 \cdot 10H_2O$ are formed.

Ammonia Soda or Solvay Process. This process was introduced by Solvay in 1863, and has been worked successfully since about 1873. It consists in reaction upon sodium chloride in a cold solution with hydrogen ammonium carbonate:

$$NaCl + NH_4HCO_3 = NaHCO_3 + NH_4Cl.$$

In conducting this process on a commercial scale, a concentrated brine solution is made by running cold water through a battery of tanks containing solid salt. The strong solution of brine is run into saturation tanks where it comes into contact with ammonia gas. When the brine is thoroughly saturated with the gas, it is run into the carbonating tower. The tower is a cast-iron cylinder 40 to 60 feet high and 5 to 6 feet in diameter. At intervals of 3 to $3\frac{1}{2}$ feet there are fixed plates with a central opening. Over these plates are placed dome-shaped diaphragms perforated with numerous small holes. The ammoniacal brine is forced under pressure into the carbonating tower through a pipe entering near the middle of the tower. The carbon dioxide, at a pressure to 25 to 30 pounds, is forced into the lower end of the tower and allowed to bubble through the many perforated diaphragms; its expansion as it enters the tower produces a cooling effect which prevents any great rise in temperature.

$$NaCl + NH_3 + H_2O + CO_2 = NH_4Cl + NaHCO_3.$$

The bicarbonate of soda, being insoluble in the ammonium chloride solution, is precipitated, drawn off, filtered, washed with cold water, and calcined

in cast-iron pans, which decomposes it into sodium carbonate, carbon dioxide, and water. The carbon dioxide liberated from the bicarbonate is pumped into the carbonating tower, and any ammonia given off is condensed and returned to the ammonia stills. The gases issuing from the carbonating tower are also condensed to recover any ammonia they contain. The temperature of the solution in the carbonating tower should be carefully controlled, 30° to 35° C. being the temperature most favorable for the action.

The soda ash produced by the calcination of Solvay process bicarbonate of soda is white and usually very pure, containing only traces of salt and sodium bicarbonate. By treating the ammonium chloride formed in the first reaction with lime, the ammonia is regenerated. The carbon dioxide is derived in part from the calcination of the sodium bicarbonate, and partly from limestone, which furnishes also the lime for the regeneration of the ammonia from the ammonium chloride. The process is more economical than the Leblanc, the product is purer, and there are no troublesome by-products like tank waste.

A by-product in the production of Solvay soda is calcium chloride solution, which finds extensive application as a dust preventive, as a brine in the manufacture of artificial ice, and as an anti-freezing solution in automobile and air-plane radiators.

Cryolite Process. The reactions involved in this process are as follows:

$$3NaF \cdot AlF_3 + 3CaCO_3 = Na_3AlO_3 + 3CaF_2 + 3CO_2.$$

The sodium aluminate resulting from this fusion is decomposed in an aqueous solution by carbon dioxide:

$$2Na_3AlO_3 + 3CO_2 + 3Na_2CO_3 + Al_2O_3.$$

The sodium carbonate formed by this process is very pure.

Sodium Bicarbonate. Most of the sodium bicarbonate on the market is produced by the Solvay process. It is one of the ingredients of baking powders, soda water, and other products that require a mild alkali.

Sodium Chloride. This important substance is very abundant in nature and is discussed in Chapter VI.

Sodium Nitrate. This compound is found in large quantities, especially in Chili. The supply, however, is becoming exhausted, and as the material is a very important one from an agricultural point of view, ways and means have been devised for producing it artificially by electrolytic methods.

Sodium Nitrite. This compound is prepared by heating sodium nitrate and metallic lead to a temperature of 450° to 500° C. It is

a valuable chemical, especially in the manufacture of dyestuffs and colors.

Sodium Sulphate. This compound is found in nature, and is also a by-product in many industries. It is discussed in Chapter VI.

Sodium Sulphite. This compound is prepared by saturating a solution of sodium hydroxide or carbonate with sulphur dioxide and then adding the same amount of sodium hydroxide or carbonate as was originally introduced. It forms large crystals used in medicine; it is an antichlor; and is the raw material for making sodium thiosulphate.

Sodium Bisulphite. By saturating sodium carbonate or sodium hydroxide with sulphur dioxide, we get the bisulphite, which comes into the market as a powder or as a concentrated solution. It is used in bleaching, as an antichlor, in paper manufacture, in the manufacture of dystuffs, and in chrome tannage.

Sodium Thisoulphate. Boiling a solution of sodium sulphite with an excess of sulphur will give the thiosulphate. It is used in photography, as an antichlor, and in the tanning of leather by the Schultz process.

Sodium Sulphide. The sulphide is made by heating a mixture of sodium sulphate, salt, and coal to a temperature of about 900° C. It is also a by-product in the manufacture of barium salts from barytes. It is used in dyeing cotton with sulphur colors, in the manufacture of dyestuffs, in unhairing hides and skins, and for denitrating artificial silk.

Strontium. One of the less common elements, this is found in nature principally as the mineral *strontianite*. It forms a series of compounds somewhat similar to those of barium.

Strontium Nitrate. This is prepared by treating the carbonate with nitric acid. It is used in the manufacture of fireworks for producing red light.

Sulphur. This element has been known for centuries, and some of the alchemists have even described compounds of it with the metals. It is known in the amorphous, rhombic, and prismatic conditions. It is of a yellow color, insoluble in water, slightly soluble in alcohol, ether, oils, and fat, but very soluble in carbon disulphide, and fairly so in petroleum ether.

Sulphur is found in large quantities in Sicily, which, up to within the past few years, practically furnished the world's supply. The recent opening up of the Louisiana deposits, however, has driven Sicily sulphur from the American market, and this country is now being supplied from the Louisiana fields. The Sicily sulphur is a surface deposit, which, on being mined, is placed in piles and heated. In this way the molten sulphur runs off from the impurities, and, when cool, is ready for the market. The Louisiana deposits are too deep to be mined, and, although these rich fields were known as far back as 1868, no means of procuring the sulphur were devised until the Frasch method was discovered. In 1902 the Union Sulphur Company started work under the Frasch process, mining about

100 tons per day. The amount, however, has steadily increased until at the present time several thousand tons are put out daily.

The Frasch process consists in sinking a shaft or well about 12 inches in diameter until the sulphur is reached, just as in boring for oil or salt. The well surrounds an iron pipe containing three other concentric tubes lined with aluminium, which are driven into the sulphur. Through the largest of the tubes, superheated water under a pressure of 100 pounds is forced. The heated water melts the sulphur, causing it to rise in the outer tube. The sulphur, however, being heavy, will not flow to the surface, so, to overcome this, hot air under pressure is made to bubble through the sulphur, thus forming an emulsion that can easily be pumped to the surface. As the sulphur issues from the tube, it is run into large wooden boxes, where it settles away from the water into an immense, hard cake. The boxes are about 20 feet wide by 100 feet long, the sides being built as the sulphur enters. Some boxes are 30 to 40 feet high. When cool the planks are removed from the sides, and the solid sulphur broken out by means of a steam shovel and loaded directly into cars or boats. The product is so pure that it needs no further refining.

Flowers of Sulphur. Sulphur, heated in a closed retort, distills, and the volatile product, passing into a cool chamber, collects on its walls in the form of fine crystals, known as *flowers of sulphur*.

Brimstone. During the refining of sulphur for flowers of sulphur, much of the distillate collects on the floor of the condensing chamber and eventually melts again. The molten sulphur is then drawn off into molds, where it hardens, forming sticks of sulphur known as *brimstone*.

Flour of Sulphur. A large amount of sulphur is passed through grinding mills and converted into a powder known as *flour of sulphur*.

Lac Sulphur. By precipitating sulphur from some of its combinations, a very light-colored product is obtained, filtered off, dried, and put on the market as *lac sulphur*.

Sulphur is used to some extent in the manufacture of sulphuric acid, for making bisulphites, sulphites, and thiosulphates, and for various other puroposes.

Sulphur Monochloride. To prepare this compound, a current of chlorine is passed over melted sulphur, heated to about 130° C. Chloride of sulphur, mixed with sulphur, distills over and is purified by redistillation. It is a somewhat oily liquid of a yellowish-brown color and suffocating odor, and boils at 144° C. In water it decomposes with the formation of hydrochloric acid, sulphur, sulphurous acid, and a small amount of sulphuric acid. Its chief use is in the vulcanization of rubber and in the manufacture of rubber substitutes.

Stannous Chloride. The hydrated salt, $SnCl_2 \cdot 2H_2O$, comes from dissolving the metal in concentrated hydrochloric acid with the aid of moderate heat. The addition of a little nitric acid also facilitates the

reaction. The solution is concentrated by evaporation, cooled, and allowed to crystallize. When dissolved in water, it undergoes partial decomposition with the formation of an insoluble oxychloride. It is a valuable mordant, is used as a weighting material for silk, and in calico printing.

Stannic Chloride. The hydrated compound comes from the mother liquor of stannous chloride by the progressive addition of nitric acid; the resulting liquid is concentrated, and the stannic chloride allowed to crystallize. The pentahydrate, $SnCl_4 \cdot 5H_2O$, may be prepared by passing chlorine through the mother liquor from stannous chloride. Its principal use is as a mordant. Most of the salts of tin are derived from scrap tin by the detinning process.

Sodium Stannate. The salt $Na_2SnO_3 \cdot 3H_2O$ may be obtained either by fusing sodium hydroxide with metastannic acid, or by boiling tin scrap with sodium plumbite. It is known as *preparing salt*, and is used as a mordant. Solutions of tin in sulphuric and oxalic acid are known in the trade for mordanting, as *tin spirits*.

Tantalum. This is one of the rare elements and occurs usually with *columbium*. It has recently acquired importance from its application in the tantalum filament for the electric lamp. The lamp consumes less than one-half the energy of a carbon filament lamp for the same candle power.

Tellurium. In the natural state this element is mixed in small quantities with gold and silver. It belongs to the same group as sulphur and forms somewhat similar compounds. It has at present no commercial applications.

Terbium. This is one of the rare elements belonging to the same group as *cerium*.

Thallium. Another of the rare elements, this has no commercial value.

Thorium. This element is found in the *monazite sands*; and its nitrate is used quite extensively in the manufacture of gas-light mantles.

Thulium. This is one of the rare earth elements and has no practical application.

Tin. This long known metal occurs in nature in many minerals as an oxide. It has a silvery appearance and is not changed in the air at ordinary temperatures. Only a limited quantity of tin was produced in this country prior to 1914, but it is now available on a very large scale. It is a common material for making cooking utensils, for lining condensers, as a constituent of many alloys, and as tin foil. It forms both stannous and stannic salts.

Titanium. This is one of the less common metals and is found principally in the mineral *titanite*. As a metal, in conjunction with iron, it makes a very tough steel. As the compound *potassium titanium oxalate*, it is a fixing agent for basic colors in dyeing cotton and leather.

Tungsten. This metal is found in certain minerals, principally *wolframite.* The metal is freed by the Goldschmidt process for reducing tungsten oxide with aluminium powder. In the metallic state it is used with iron for making high-speed steel. In the colloidal form it is now in great demand for making the tungsten electric lamp filament; and in the form of sodium tungstate, as a fireproofing on wood and fabrics. The requirements for this metal within the past five years have increased a great deal, owing to its use in automobiles and air planes.

Uranium. This is one of the rarer elements and is found in the mineral *pitch-blende.* Its oxide gives a yellow fluorescence to window glass.

Vanadium. Found in the mineral *vanadinite,* it is used to some extent with iron in producing a vanadium steel. Certain of its salts are common in dyeing and printing, while its oxides are known in the manufacture of glass and pottery.

Xenon. This is one of the very rare elements occurring in the atmosphere to the extent of about one part in forty million.

Ytterbium. The source of this rare element is the mineral *gadolinite.*

Yttrium. This is a rare element also occurring in the mineral *gadolinite.* It is used in the filament of the Nernst lamp.

Zinc. The form usually found in nature is the sulphide, contained in many minerals. The sulphide, on roasting, is converted into the oxide, and sulphur dioxide escapes. The oxide may then be readily reduced to the metal by heating with carbon in a muffle furnace. Metallic zinc has a grayish white appearance. It is used in making zinc-coated wire and iron, the latter being known as *galvanized iron.* It forms various alloys, and has many other applications.

Zinc Oxide. This compound, of value in the manufacture of paint, is discussed in Chapter XIV.

Zinc Sulphate. *White vitriol,* $ZnSO_4 \cdot 7H_2O$, is made by dissolving scrap zinc in dilute sulphuric acid. Upon evaporation, a white, crystalline substance separates. It is used to some extent in calico printing and in dyeing, as a drier for linseed oil, as a disinfectant, and as an astringent.

Zirconium. This rare earth was used in preparing the first incandescent mantles.

Matches. Chemical matches were introduced in 1807 and known as "chemical tinder." They were made by saturating a portion of the splint in melted sulphur, and the head was a mixture of potassium chlorate and sugar. To light the match it was brought in contact with sulphuric acid, which caused a rapid decomposition of the chlorate, and kindling of the sulphur and sugar. From this primitive yet scientific discovery, the modern friction and safety matches have been evolved.

Double Dip Friction Match. Perfectly dry, white pine blocks are cut into $3\frac{3}{8}$-inch lengths. These blocks are then fed into the cutting machine

(Fig. 120), so that the grain stands in a vertical position to the knife, which is attached to a plunger and cuts forty match splints at a single stroke. To completely dry the splints, they are automatically forced into the openings of perforated iron plates, conveyed by an endless chain over a series of heaters. Adjoining the heater a spring arrangement forces out any thin or poor splints. The plates, now carrying only perfect match sticks, pass over a trough of paraffin in such a manner that one-quarter of the stick becomes impregnated. They next pass over the composition rollers, where a small amount of the composition is deposited on the end of each splint. The composition of the first dip consists of potassium chlorate, glue, flint, and filler (such as clay for body). In order that the first dip may have time to dry, the plates are made to travel up and down through a series of wheels, and are then given a second dip on a machine similar to the first. The composition of the second dip consists largely of phosphorus, chlorate of potash, glue, and filler. The finished match is now carried back to where it was cut, is punched out into troughs, and carried to the packers. The plate is refilled and the journey repeated. The advantage of the double dip match over the other forms is that the danger of a flying-off head is eliminated. The tip or second dip ignites on friction, the heat produced being sufficient to ignite the first dip, both of which burn quietly.

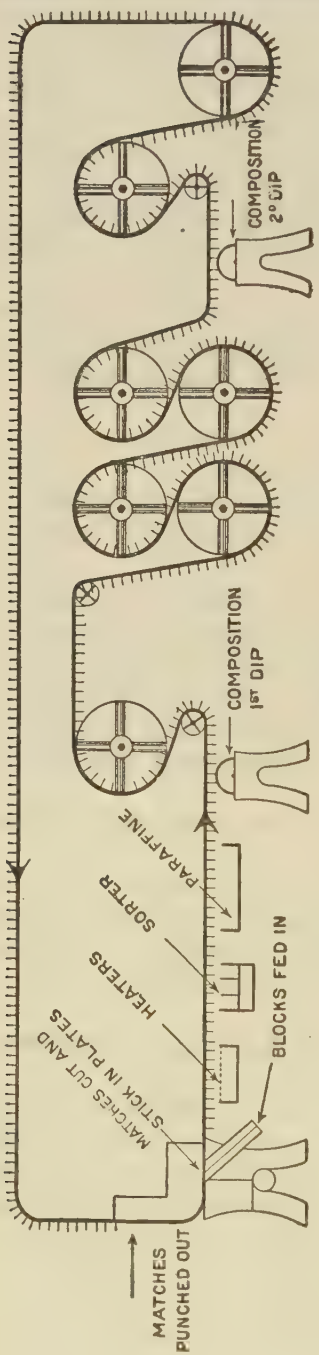

Fig. 120.

The machine used for double dip matches is 96 feet long, contains 1600 plates, takes one hour for the complete operation, and makes 8,000,000 matches in ten hours.

Single Dip Matches. The manufacture of matches by this process is the

same as by the foregoing, except that the single dip makes it simpler. The composition of these matches consists of glue, potassium chlorate, phosphorus, flint, and filler.

Safety Matches. These are made in a manner similar to friction matches, except that the phosphorus is not present on the head of the match. In order to ignite the match, it must be rubbed over a surface coated with phosphorus, which thus acts in a manner similar to the second dip on a friction match.

CHAPTER VIII

CHLORINE AND ALLIED PRODUCTS

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Raw Materials. The primary raw materials of the chlorine industries are the alkali chlorides, common salt (chloride of sodium) and potassium chloride. Common salt of high purity is everywhere available at moderate cost, the most objectionable impurity being calcium sulphate. The cost of salt is about $4 per ton f.o.b. works, but at the salt mines or brine wells it is much less. Potassium chloride occurs in commercial quantities only at the Strassfurt deposits in Germany. It is not usually as pure as common salt and contains considerable amounts of sodium and magnesium salts. Much potassium chloride is treated electrolytically in Germany for the production of caustic potash, the chlorine being delivered from the cells practically free of charge to the manufacturer, since the value of the caustic potash is sufficient to cover all the manufacturing costs and still leave a profit. This cheap chlorine is largely responsible for the rapid rise in the manufacture of bleaching powder and chlorine products in Germany.

A secondary raw material is hydrochloric acid, resutling from the action of sulphuric acid upon common salt. It was formerly almost a waste product of the Leblanc process for manufacturing sodium carbonate, and is still available in England in enormous quantities at a very low price.

Sodium chloride is a very stable compound. Its heat of formation in the solid state is 97.7 cals. (kilogram calories) per gram equivalent (58.5 grams):

$$NaCl + 97.7 \text{ Cals.} = Na + Cl.$$

In liberating the chlorine this energy must be supplied in the form of heat by electricity or by the chemical energy accompanying the formation of other compounds of sodium. In hydrochloric acid (heat of formation as gas+22 cals. in aqueous solutions+38.0 cals.) the chlorine is not so powerfully bound and less energy or power is necessary for its liberation.

The manufacture of caustic soda and chlorine directly from common salt has been accomplished only electrolytically. Theoretically the simplest process is the electrolysis of fused salt and conversion of the sodium to sodium hydroxide by reaction with water.

One gram equivalent of solid sodium chloride requires for decomposition into sodium and chlorine 97.7 cals. This is equivalent in electrical energy to 407,084 joules (joules = amperes × seconds × volts) 1 joule = .00024 cal., therefore 97.7 cals. = 97.7 ÷ .00024 or 407,084 joule). We know from Faraday's law that for the electrolysis of 1 gram equivalent of any substance there are necessary 96,540 coulombs (coulomb = ampere × seconds). The electrical pressure must therefore be at least $\frac{407084}{96540} = 4.21$ volts in any system in which fused salt is the electrolyte and sodium and chlorine the primary products. This is the theoretical minimum. If electrical energy is consumed in overcoming the resistance of the bath, dissipated in the form of heat, or used up in the formation of by-products, more energy will be required, as is indeed always the case in actual practice. The theoretical minimum, however, serves as a measure. If, for instance, in the electrolysis of fused salt 7.00 volts are required, the volt or pressure efficiency is 60 per cent. While a high energy efficiency is desirable it is by no means all important. Power is only one item of expense and is often overbalanced by the cost of labor, maintenance, and materials.

Sodium chloride melts at 772° C. (dull red heat) and at this temperature is a good conductor of electricity. On passing an electric current of sufficient voltage through fused salt gaseous chlorine is liberated at the anode and liquid metallic sodium at the cathode. The sodium, being lighter than salt, floats up through the bath, and unless immediately removed recombines with the chlorine or oxidizes in the air. Fused salt acts strongly upon most materials, and the construction of a suitable container is a serious problem. The hot chlorine also acts upon metals and many anode materials. These various difficulties have been overcome in the Acker process, as follows:

Acker Process. In the Acker process, Fig. 121, solid salt is fused by passing through it a current of very high density. Chlorine is liberated at the anodes of Acheson graphite and is drawn off by a slight suction into brick conduits. Sodium is liberated at the cathode, a shallow body of molten lead, with which it immediately alloys. This alloy is fluid as long as the percentage of sodium is very low. The body of molten lead is kept in continuous motion in one direction and passes through a short connecting channel under the hearth to a second compartment called the well. It is here elevated by means of a sort of steam injector, which consists of a vertical cast-iron pipe dipping into the well and pointed upward. The well has a curved cast-iron cover. On admitting steam, the lead sodium alloy is projected upward against the face of the cover and decomposed into metallic lead, caustic soda, and hydrogen. The products are deflected downward into a third small compartment, the caustic chamber. Here the lead sinks by gravity and flows back into the cell to take up more sodium and go the round anew. The caustic soda, being lighter, collects in an anhydrous condition at the top of the caustic chamber and overflows from a spout into a col-

lecting vessel. Any excess of steam with the hydrogen, which burns quietly, escapes at the same point. The action is entirely continuous. The rate of flow of the cathode lead is controlled by the rate of steam supply, which is usually a little greater than that theoretically necessary to convert the metallic sodium into hydrate. The bath of electrolyte is kept up to volume by periodically shoveling in solid salt. The cell or furnace is made of cast-iron, that portion which contains the salt being lined with two rows of magnesia or ordinary firebricks laid in without bond. The molten salt penetrates between the cracks and freezes in the outer layer, making the lining impervious. Each cell is about 3×6 ft., and carries four anodes having an effective surface of about 3 sq. ft. in all. The under surface of the anodes are grooved to prevent the chlorine accumulating upon them, which would raise the resistance. The current is very high, 8300-8500 amperes, a current density of 2800 amperes per square foot at the anodes.

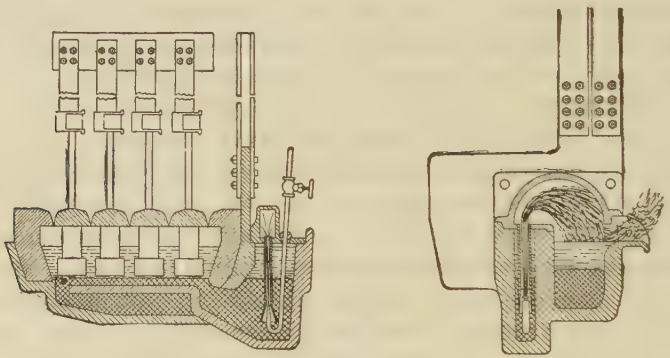

Fig. 121.

The voltage is about 6.5 volts under normal operating conditions. The output of each cell is about 550 lbs. anhydrous sodium hydroxide and 495 lbs. chlorine per 24 hours. The caustic is very pure. It contains 1 per cent total impurities (a little salt which gets in mechanically and a little carbonic acid taken up from the air). It is collected in large pots holding from 10 to 13 tons, where it is kept molten to allow impurities to settle out and is treated with a little sodium hyposulphite to destroy traces of sodium manganate, etc., which gives it a green color as it runs from the cells. While still liquid, it is bailed into the cast-iron drums in which it is sold.

The good features of the process are the high output per cell, many times larger than that possible with any wet process cell of similar size; the saving of the expense of boiling down weak caustic liquor, of dissolving salt, etc. The drawbacks are the somewhat high voltage necessary and the dilution of the chlorine, which is drawn off mixed with about 20 or 30 times its volume of air. This weak chlorine is well adapted for certain purposes but not all. Its use in manufacturing bleaching powder requires mechanical absorbers.

The anodes withstand the chemical action of the chlorine remarkably well, but are somewhat liable to mechanical injury from careless handling. The furnace castings have a life of seven or eight months under favorable conditions, but are in danger of being cracked at the time of starting or shutting down, unless this is done very gradually.

The electrolysis of fused salt proceeds best at temperatures not greatly exceeding its melting-point. At higher temperatures a mist, supposed to consist of subchloride, Na_2Cl, diffuses upward from the cathode, reducing the current efficiency very greatly.

Ashcroft Cell. Ashcroft has also devised a cell for the electrolysis of fused common salt. His cathode of fused lead is circulated by the action of a powerful electromagnet. The lead-sodium alloy is withdrawn and is made the anode in a second cell. After plating out its sodium content as metal in a bath of caustic soda, the lead is returned to the primary cell.

Chlorine is also produced by the electrolysis of fused zinc chloride which melts at a low temperature. Carbon anodes and a cathode of fused zinc are generally used. The process has been in successful operation in England for a number of years and forms an important feature of the Swinbourne and Ashcroft process for treating complex ores. It is necessary to keep the zinc chloride entirely free from oxide. In this point lies the chief difficulty of the process.

Electrolysis of Aqueous Salt Solution. The reactions occurring in the electrolysis of an aqueous solution of salt are very complicated. On passing a current between insoluble electrodes the primary action is of course the liberation of chlorine at the anode and sodium at the cathode. The chlorine escapes from the system chiefly as a gas, but a small portion dissolves in the electrolyte and begins to diffuse toward the cathode. The sodium liberated at the cathode immediately combines with water, forming caustic soda and liberating hydrogen as a gas.

$$Na+H_2O=NaOH+H.$$

The caustic soda then begins to diffuse toward the anode, and as soon as chlorine from the anode and sodium hydroxide from the cathode meet hypochlorites are formed.

$$2NaOH+2Cl=NaOCl+NaCl+H_2O.$$

The action is further complicated by the caustic soda and sodium hypochlorite both beginning to carry current, and electrolyzing:

$$2NaOH=2Na+2OH.$$

The hydroxyl ions discharge at the anode forming water and oxygen, which escape with the chlorine or act upon the anode material and dissolved products about the anode. The hypochlorite is likewise decomposed, and the formation of chlorate in the electrolyte begins. This again carries current. Should no means be provided to keep the anode and

cathode products separate, the current efficiency, which was at the beginning 100 per cent, drops to a very low figure. In the direct formation of hypochlorites and chlorates by electrolysis, the combination of the anode and cathode products are essential, but in the production of sodium hydroxide and chlorine, this must be, as far as possible, prevented. This has been achieved by a variety of means, giving rise to a number of successful but very different processes. The necessity of obtaining caustic soda of as high a concentration as possible has also had its influence on the types of apparatus devised. The reaction:

$$NaCl+H_2O=NaOH+H+Cl,$$

represents an expenditure of energy equal to 53 cals. By simple calculation the critical or theoretical minimum voltage is found to be 2.29 volts, much lower, therefore, than the critical voltage for fused salt.

According to the means adopted to prevent or minimize the interaction between the primary anode and the cathode products, the processes may be divided into three classes:

A—Mercury cathode;
B—Diaphragm;
C—Bell type.

Castner-Kellner Process. This may be considered as the type of mercury cathode processes, of which it is the oldest and most generally successful example.

The Castner cell, Fig. 122, consists of a slate box 4 ft. long, 6 ins. deep, and 4 ft. wide, divided into three compartments by partitions extending to

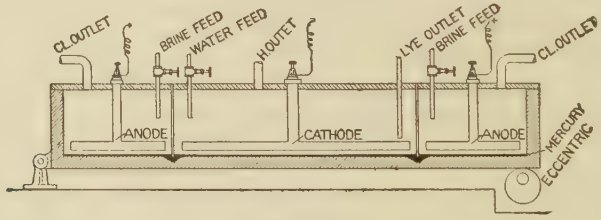

Fig. 122.

within $\frac{1}{16}$ of an inch of the bottom. These compartments are kept separate by a layer of mercury covering the entire bottom of the apparatus. The outer compartments are filled with strong salt solution and the center compartment with pure water. In each outer compartment there are several T-shaped anodes of Acheson graphite with the lower surface within 1 in. of the mercury. In the center compartment is an iron grid which serves as the cathode. The cell is pivoted at one end and rests on an eccentric at the other, which raises and lowers $\frac{1}{2}$ in. once a minute, imparting a rocking motion and causing the mercury to flow backward and forward between the compartments. On passing the current the salt in the outer

compartments is decomposed, liberating chlorine at the anodes, which is drawn off by slight suction. Sodium is liberated at the intermediate cathode of mercury and alloys with it. The sodium mercury alloy flows into the center compartment, where it plates out sodium at the iron cathode. The sodium instantly combines with the water, forming caustic soda and hydrogen. The caustic soda dissolves while the hydrogen is allowed to escape into the room. Part of the current must be shunted off before passing to the final iron cathode. Only 90 per cent of the charging current is allowed to pass through the discharging cell, otherwise mercury would pass into solution in the cathode compartment, forming HgO, destroying the continuity and clean metallic liquid character of the mercury, and causing a heavy loss of this expensive material.

The salt solution flows through the anode compartment continuously, being brought back to its original high concentration by the addition of salt outside the cell, and then returned for re-use. As the sulphates in the brine accumulate, they are from time to time removed by precipitation with barium chloride. The water in the center compartment is left until the caustic soda has raised its gravity to 1.3. The caustic soda solution is then run off and replaced by fresh water. The lye is boiled down in cast-iron pots until anhydrous, and is packed molten into iron drums. It is very pure, often 99 per cent actual sodium hydroxide.

The cells are inexpensive to construct and last indefinitely, likewise the iron cathodes. The anodes last a year or more. The current at the anode is about 630 amperes per cell, of which 10 per cent is shunted off before discharging in the cathode compartment. The voltage is about 4.3. The current efficiency is nearly 90 per cent, energy efficiency 47 per cent. The current density at the anode is about 150 amperes per square foot, and at the mercury, 110 amperes per square foot. The current which can be used is limited by the necessity of keeping the temperature of the cell below 40° C., at which point chlorate begins to form. Each cell decomposes per twenty-four hours, 65 lbs. sodium chloride, forming 44 lbs. sodium hydroxide, and liberating 39.4 lbs. chlorine. The output per H.P. per twenty-four hours is 12.0 lbs. sodium hydroxide and 10.8 lbs. chlorine.

The two factors which have most largely contributed to the success of this type of cell are:

(1) The rocking mercury cathode.

(2) The cathode shunt.

Each Castner cell requires about 150 lbs. of mercury, which it is essential to keep bright and clean, and of which there must be no loss. The mercury is not dissolved by the brine as long as it is electrically negative and does not oxidize in the center compartment unless denuded of sodium; hence the necessity of a higher charging than discharging current.

Whiting Cell. A cell of a somewhat similar kind is that of Whiting, in operation at Rumford Falls, Me. Here the mercury is circulated by means of a pump, and the decomposing compartment is not in electrical

contact, i.e., mercury-sodium is formed and is removed from the system mechanically, decomposed outside the circuit, and the denuded mercury returned. The voltage is somewhat higher than that of the Castner cell. The current efficiency is high.

The older mercury cells operate at comparatively low current densities on the mercury cathode, because it is necessary to have the amalgam content of the mercury low to keep it fluid. The amalgam, being specifically lighter than the mercury, tends to collect at the surface in the anode compartment where it is formed, and the more fluid mercury passes through the seal into the decomposing compartment first. Working with higher current densities than about 110 amperes per square foot, there is a tendency to form crusts of very rich and solid amalgam which do not pass through the seal, but react with the brine and decrease the efficiency of the cell. With potassium chloride as the electrolyte this is very marked, because potassium forms much more solid amalgams than sodium at equal concentration. With potassium a current density of about 20 amperes cannot be greatly exceeded.

All the dirt in the salt collects on the surface of the mercury at the bottom of the cell, and very pure or carefully purified brine must be used to keep the mercury from becoming foul. These difficulties have been overcome in the Wildermann cell, in operation on a large scale since about 1911.

Wildermann Cell. The Wildermann cell is constructed of iron covered with ebonite that contains graphite, and in which the sulphur is sufficiently high to completely saturate the double bonds of the rubber molecule. The composition is that of the empirical formula $C_{10}H_{16}S_2$ plus 10 per cent of graphite (33 parts sulphur, 57 parts Para rubber, 10 parts finely divided very pure graphite). Such ebonite is sufficiently flexible and elastic, can be made to adhere perfectly to iron, and is very resistant to both chlorine and caustic alkalies.

The cell (Fig. 123) consists of a decomposing compartment (*a*) and a combining compartment (*b*) separated by a vertical partition composed of superimposed troughs containing mercury with free surfaces exposed in the combining and decomposing compartments. The inner decomposing compartment contains the anodes (*C*) and saturated solution of sodium or potassium chloride. The outer combining compartment contains caustic solution of 20 or 22 per cent concentration. The current passes from the anode through the brine to the mercury and from here back to the dynamo or the next cell in series. Alkali metal is thus deposited by the current on the surface of the mercury and alloys with it. Stirrers (*d*) provided with teeth (*e*) dip into the mercury, mix the alloy with it, and carry it to the bottom of the troughs. The troughs are of such shape that the alloy is brought below the mercury of the caustic side. Being specifically lighter then mercury, it immediately rises by buoyancy to the surface of the mercury on the caustic side.

From the mercury it passes into the caustic solution with great rapidity by reason of the small carbons (*f*), which are in electrical contact and form a local battery with the amalgam, so that the mercury at the top is kept practically free from alkali metal.

The cells are run with either sodium or potassium chloride at current densities on the mercury of from 300 to 700 amperes per square foot, the voltage running from about 5 to 8. Operating as low as 110 amperes per square foot, the voltage is about 4.

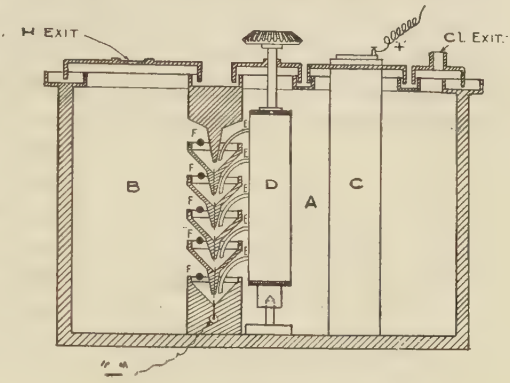

FIG. 123.

In one installation 6000 ampere cells are used and a current density at the mercury of 330 amperes per square foot. These cells occupy about 30 square feet floor area each and produce 440 lbs. caustic soda and 400 lbs. chlorine each per 24 hours. This is about 10 lbs. caustic soda and 9 lbs. chlorine per horse-power per 24 hours. With expensive power it would be more profitable to run at a lower density and voltage, under which conditions the yield per horse-power would be greater.

The anodes are of much greater surface than the cathodes, and the anode current density therefore very much less than at the mercury. This makes possible the use of artificial graphite anodes, otherwise more costly platinum anodes would have to be used.

Diaphragm Processes. In cells of this type the anode and cathode are separated by a porous partition, which in most successful cells is in close contact with the cathode. Concentrated salt solution is usually fed into the anode compartment and flows toward the cathode under slight head. The diaphragm controls and regulates the forward motion of the salt solution and retards the backward flow of the caustic soda formed at the cathode. The caustic liquor formed at the cathode is drawn off continually. If the rate of flow is high the crude cathode liquor contains much salt, and the percentage of sodium hydroxide is low; if the flow is slower the concentration in sodium hydroxide will be higher and the lye will contain less salt, but there will be greater diffusion of sodium hydroxide backward through the anode compartment, with recombination, etc., and loss in electrical efficiency.

Allen-Moore Cell. A widely used cell of this type is the Allen Moore. This consists of a central anode compartment separated from the cathodes of perforated iron by diaphragms of asbestos cloth. Brine is fed into

the anode compartment, being maintained at constant head by a float valve.

The caustic soda formed at the cathode is carried away into the vacant cathode compartment by the flow of liquid through the diaphragm and cathode caused by this pressure. In section the cell is similar to the Townsend cell, Fig. 124, except that the outer cathode compartments which contain kerosene in the latter are empty. The caustic liquor as it flows away from the cathode compartments carries a variable percentage of salt and caustic soda, depending upon the particular operating conditions which vary with local conditions and costs. It is concentrated in multiple effect evaporators. The salt largely separates at an early stage in concentration and is removed " fished out " and if the local price of salt is high, slight adhering alkali is removed by acidifying with hydrochloric acid or other suitable means. Graphite anodes are preferable when obtainable, but at the present time anodes of retort carbon or fused iron oxide are largely employed and render excellent service. To insure maximum life and efficiency of the diaphragms it is important to have the brine as pure as possible, and it is common practice to purify the brine supply before it is fed into the cell. Calcium and magnesium salts are particularly objectionable, as they form insoluble hydroxides of lime and magnesium at the cathode which plug the asbestos diaphragm in a short time.

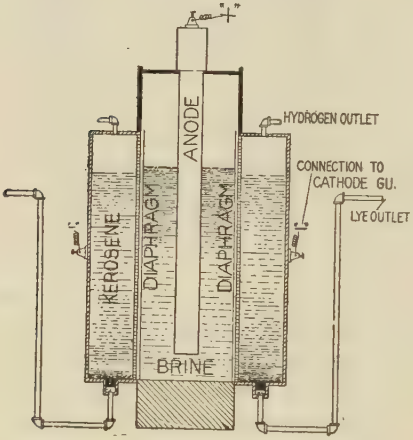

Fig. 124.

The Nelson cell is of a somewhat similar type. In this cell an atmosphere of steam is maintained in the cathode compartment.

Hargreaves-Bird Process. In the Hargreaves-Bird process the caustic is converted to carbonate at the cathode and its backward diffusion thus prevented. The cell consists of a cast-iron box 10 ft. long, 5 ft. high, and 2 ft. wide. The cathodes of copper gauze support the diaphragm of an asbestos, silicate of soda, Portland cement composition, and divide the cell into three compartments. The inner compartment contains the anodes of retort carbon, with lead connections which are protected by a coat of cement. The diaphragm is sufficiently impervious to prevent the brine with which the inner compartment is filled to flow through, en masse, but permits electrolysis to take place through it. The space between the outer cathode walls and the walls of

the cell is empty of liquid. In it a mixture of steam and carbon dioxide is blown which forms carbonate of soda solution on the walls of the cathode which trickles away. The chlorine liberated at the anode is pumped out of the anode compartment, along with the brine, the chlorine is trapped off, the brine brought back to its original concentration by saturating with more salt and returned by a stoneware pump to the cell. The current in the Hargreaves-Bird cell is high, voltage low, 3.3 volts, but it labors under the disadvantage of producing low-priced sodium carbonate instead of the more valuable sodium hydroxide, and seems to be losing ground in competition with the cells producing caustic. The output per cell per twenty-four hours is, sodium carbonate 170 lbs., chlorine 113 lbs., per H.P. per twenty-four hours, sodium carbonate 18 lbs., chlorine 12 lbs.

Townsend or Hooker Cell. In the Townsend cell, which is shown in cross-section in Fig. 124, the anodes are graphite, the cathodes are perforated iron plates, separated from the anode compartment by vertical diaphragms which adhere closely to the iron cathodes. The outer surfaces of the cathode plates are bathed in kerosene in the cathode compartments. The anode compartment is kept filled with brine. A hydrostatic pressure is maintained whereby a portion of the brine flows slowly from the anode into the cathode compartments. As soon as current is passing, this escaping brine is charged with the caustic soda formed by electrolysis. Passing through the perforated iron plates it meets the kerosene bath and forms oily drops which detach from the walls and sink to the bottom of the kerosene out of electrical or chemical contact with the system, and is continuously removed. The spent anode brine is pumped continuously from the anode compartment to a tank where it is saturated with salt and the chlorine trapped off. It is then returned to the cell. The cells are made in rather large units and carry from 4000 to 6000 amperes per cell. The composition of the cathode liquor varies with the rate of percolation. With the rate found most advantageous in practice the composition is about 150 grams sodium hydroxide and 213 grams sodium chloride per liter, with lower hydrostatic pressure and reduced percolation—the composition can be brought to sodium hydroxide 250 grams, sodium chloride 140 grams. This cell can be run at very low voltage, as low as 3.5, with a current density of 70 amperes per square foot at the anode, but with increased current density (140 amperes per square foot at the anode), the voltage rises to about 4.7. While the yield of sodium hydroxide and chlorine per H.P. is less at the high density the output per cell is greater, and it has been found on the whole more economical to sacrifice power to greater output per unit of plant.

Baekeland Diaphragm. The diaphragm, which is the invention of Dr. Baekeland, consists of asbestos cloth filled with a special paint made of a mixture of oxide of iron, asbestos fiber and gummy iron hydroxide.

The diaphragms become clogged in five or six weeks, so are removed and given a fresh coat of the paint. This diaphragm is very economical and efficient.

All the diaphragm cells thus far described have vertical diaphragms. The advantages are simple construction both of the cell and the diaphragm, easy accessibility of the inside of the cell for cleaning, and less floor space for a given output. The Billiter-Siemens is the first of recent commercial cells to use a horizontal diaphragm. The advantages of this construction are that the diaphragm is more slowly attacked chemically because it is always to a certain extent saturated with the alkali which migrates upward from the cathode; and the hydrostatic pressure on the diaphragm is uniform at all points not varying with the height as in vertical diaphragms. This insures a more uniform flow of liquid through and more efficient checking of the migration of caustic towards the anode.

Billiter-Siemens Cell. The Billiter-Siemens cell (Fig. 125) is long, narrow and trough shaped. It contains an inner vessel or bell (*A*) with granite side walls or walls of boiler plate with a lining of cement on the inner surface. The bell is closed at the bottom by a diaphragm (*BC*), the latter resting on a supporting lattice work cathode (*D*) of iron or nickel wire which is fixed to the bell and arched in order to permit the hydrogen bubbles to escape at the channel *E*. The anodes (*F*) of graphite are arranged parallel to the cathode. The bell is supplied with electrolyte (sodium or potassium chloride solution) through the supply pipe (*G*) to a definite depth. It rests in an outer vessel (*H*) of iron which is at first empty, but the diaphragm is permeable to the brine and the latter arrives at the cathode as a solution containing caustic and excess salt. The caustic solution is retained until it overflows at the escape pipe (*J*) so arranged that (*H*) is kept filled just sufficiently to wet the cathode.

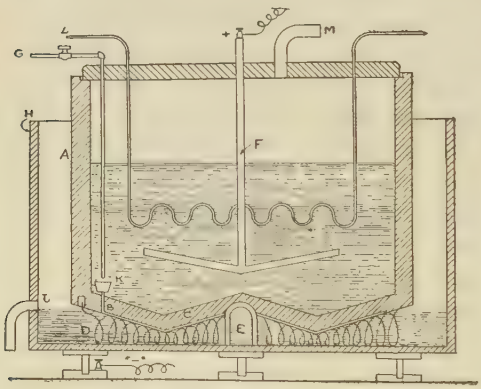

FIG. 125.

The diaphragm consists of a sheet of asbestos (*B*) kept in position by a frame (*K*) and wedges, over which is spread a thin layer (*C*) of precipitated barium sulphate and asbestos fiber. The barium sulphate is precipitated in presence of the asbestos fiber from a hot solution containing salt. A uniform mixture is thus obtained, and by precipitating hot there is no subsequent change in the size of the sulphate grains in the cell which is operated hot. The brine is heated by hot liquid kept

circulating through the stoneware pipes (*L*). The chlorine is drawn off through the exit pipe (*M*). The cathode is in electrical contact with the iron bottom of the cell, which rests on I-shaped girders which are insulated from the ground. The negative leads are connected to the bottom of the cell or the girders.

The internal heating arrangement materially reduces the voltage and power consumption. This with the special diaphragm construction are the distinctive features. The cells are constructed up to 3000 amperes capacity and work with a current efficiency of 95 per cent. The working temperature is preferably 70 to 85° C. The best current density at the diaphragm is about 45 amperes per square foot. At current densities above 70 disintegration of the diaphragm sets in. The concentration of the caustic liquor varies with the voltage. At a voltage of 3.66 it is about 130 grams NaOH per liter.

In all the diaphragm processes the primary cathode products consist of a solution of caustic soda and salt. This is boiled down in cast-iron vessels, usually under a vacuum with triple or quadruple effect. At a moderate concentration most of the salt separates out, the caustic soda remaining in solution. The salt is removed (fished), and after neutralizing the small amount of entrained caustic with hydrochloric acid, goes back into the process.

The anode liquor is very destructive to carbon or graphite electrodes if it becomes alkaline; this is guarded against, in some processes, by the addition of a little hydrochloric acid at the anodes. Other diaphragm processes which space does not permit the description of are the Roberts, using a diaphragm compounded of anthracite coal, the Leseur, the Outherine Chalandre, etc.

Bell Process. In the bell processes, of which there are several, combination of the anode and cathode products is prevented without the use of a diaphragm by suspending the anodes in bells, admitting the brine at the anode at such a rate that it flows past the cathode faster than the cathode products can diffuse upward. The apparatus is very simple, but current density is low and the size of the cells is small. The cathode liquor is very weak in caustic soda and very high in salt, necessitating boiling down a great quantity of liquid. In Aussig and other parts of the continent of Europe, where fuel and labor are cheap, it has, notwithstanding, been commercially successful. A simple type of cell is shown in Fig. 126.

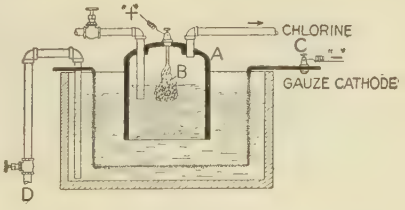

FIG. 126.

A, bell with chlorine outlet tube, and trapped brine feed pipe; *B*, anode of retort carbon; *C*, cathode of iron gauze; *D*, overflow syphon for cathode liquor.

Billiter-Leykam. The Billiter-Leykam cell is an important advance

in cells of this type. In this cell the cathodes are hooded to collect the hydrogen and are placed directly underneath the bell jar and not around its sides as in the Aussig cell. The advantage gained is that there is no change of direction in the flow of current and flow of electrolyte at the edge of the bell with consequent irregularity. Because of the uniform current density and flow of electrolyte, brine can be fed at just sufficient speed to overcome the diffusion and migration upwards from the cathode. The motion of the electrolyte is directly opposed to the current lines till it has passed the cathodes. The current density is very high for cells of this type (up to about 60 amperes per square foot at the anode). Strong caustic liquor is produced (12 to 15 per cent NaOH). The current efficiency is high (95 per cent). Comparatively large units can be constructed. One plant consists of 1200 ampere cells each producing about 100 lbs. caustic soda and the corresponding amount of chlorine per twenty-four hours. The voltage is low, 3.1 to 3.2 volts. The electrical efficiency is therefore probably the highest of any commercial cell. They are preferably internally heated and operated at a temperature of about 85° C. They require very little attention since when once started there is almost nothing to get out of order. The floor space required is, however, large. A 1200-ampere cell is about 20 ft. long, 4 ft. broad, and 4 ft. high and requires 24 anodes of graphite 40 in. by 7 ins. by 2 ins. The cathodes are of T-iron slightly inclined and enclosed in woven asbestos tubes which carry the hydrogen away, but interpose very little resistance to the current or to the electrolyte, much of which latter flows between the cathodes which are spaced one-quarter inch apart. Fig. 127 shows in sketch a cross-section of the Billiter-Leykam cell.

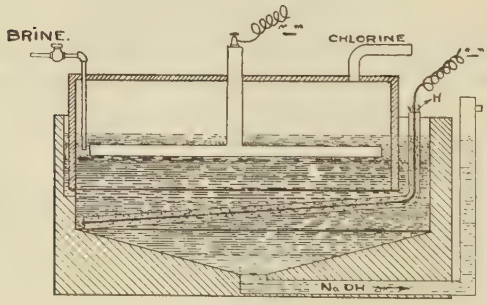

Fig. 127.

Platinum anodes have been successfully used in the electrolysis of salt; the chief objection is their high original cost. There is some gradual loss of platinum, but in a properly designed plant the expense need not exceed nine or ten cents per 100 lbs. chlorine produced.

For each 71 lbs. of chlorine there are formed 2 lbs. of hydrogen. Up to the present this has in most cases been simply allowed to escape. One plant uses it to make very pure hydrochloric acid by burning it in an atmosphere of chlorine in fused quartz burners. Increased outlets for hydrogen have arisen in the last few years in the hydrogenation of oils and fats, synthesis of ammonia, for balloons and welding. While the value is not very great it is still probable that the hydrogen pro-

duced in most electrolytic chlorine plants will be more and more utilized in some such ways as time goes on.

The following balance sheet shows the cost per twenty-four hours of a plant producing 12,670 lbs. sodium hydroxide and 12,500 lbs. chlorine, using one of the diaphragm processes:

Balance Sheet

Power-cells, 1200 H.P., at $17 per horse-power year	$55.89
Power-motors, 25 H.P., at $17 per horse-power year	1.16
Salt, 23,000 lbs. at $4.50 per ton	51.75
Superintendence	20.00
Labor, 14 men, at $2.25	31.50
Coal, 8 tons, at $3.50	28.00
Depreciation and taxes	23.95
Maintenance and repairs	31.25
Drums, 27, at 91c	24.57
Debit	$268.07
Credit.	
12,500 lbs. chlorine, at .01	$125.00
Cost of 12,670 lbs. caustic soda	$143.07

Chemical Processes. Of the purely chemical processes for preparing chlorine two survive, the Weldon and the Deacon processes. Both use muriatic acid as the source of chlorine. Because of the expense incident to transporting this acid, wherever chlorine is produced in a large way chemically, the acid is made on the spot.

Weldon Process. Muriatic acid is oxidized by manganese dioxide, liberating chlorine at a moderate temperature.

$$MnO_2+4HCl=MnCl_2+2H_2O+Cl_2.$$

The primary source of the dioxide is the mineral pyrolusite, which contains from 50 to 70 per cent of manganese dioxide. High manganese dioxide content is very desirable for chlorine manufacture, and less than 57 per cent renders the mineral unsuitable for the purpose. The muriatic acid should be of high concentration, 30 per cent upward of actual hydrochloric acid and fairly free from sulphuric acid, otherwise the regeneration of the manganese dioxide becomes difficult or impossible and the process unprofitable. The generation of chlorine is always conducted in stoneware stills (firebrick, sandstone), etc., which may be of rather variable design. In starting with pyrolusite, the mineral is placed in the still first, on a raised platform, then the acid, preferably warm, is run in gradually, finally the still is moderately heated by blowing in a current of live steam. The muriatic acid acts on the dioxide until its concentration is reduced to about 5 per

cent actual hydrochloric acid. With recovered manganese the acid is utilized down to about 2 per cent. The chlorine is evolved in a steady stream and is conducted by lead or stoneware pipes to the point of utilization. Since pyrolusite is fairly expensive, the profitable production of chlorine necessitates the recovery of the manganese from the spent still liquor. The Weldon process, which is the most successful method of doing this, is based on the fact that freshly precipitated manganous hydroxide suspended in a solution of calcium chloride is easily converted into peroxide by a current of air forced through the liquid, if there be present an excess of lime. The excess of lime is essential.

Process of Recovery. The spent liquor from the still is run into a neutralizing well, where it is treated with ground chalk, or better with regenerated manganese mud. The free hydrochloric acid is thus neutralized, and any iron present is precipitated. The residual chlorine dissolved in the liquor is carried off along with the evolved carbon dioxide to a tall chimney, whence it escapes, or it may be removed by passing through a scrubbing tower.

The neutralized liquor is allowed to settle for a few hours, when the clear solution is run into the oxidizers. These are iron tanks 10 ft. in diameter and 30 ft. high, with a perforated pipe at the bottom through which air is admitted under pressure.

The oxidizer is about half filled with manganese liquor (averaging 60 grams per liter manganese as manganese dioxide). By means of live steam the liquid is heated to 55° C. Lime water, prepared by slaking pure lime very low in magnesium, is then run in till all the manganese is precipitated as manganous hydroxide. Then $\frac{1}{4}$ to $\frac{1}{3}$ excess is added. Meanwhile the air is blowing full blast through the liquor. The liquor is at first yellow but gradually becomes black. The first blowing is continued three to five hours, till the liquor, which was at first strongly alkaline, is nearly neutralized and no more manganese dioxide forms.

About $\frac{1}{4}$ as much manganese liquor as originally used is then added, and blowing is continued for another two hours.

The mud is then run into settlers, where it remains until the precipitate subsides. The clear supernatant solution of calcium chloride is then run off as a waste.

The current of air must be very powerful, otherwise what is known as a stiff batch is liable to form. If there is not sufficient excess of lime the oxidation is only partial and what is known as a red batch is formed. This consists chiefly of Mn_3O_4.

About 168 cu.ft. of air are required to produce 1 lb. of manganese dioxide.

The use of recovered manganese mud greatly simplifies the production of chlorine. Very much larger stills, usually pentagonal, are used. Muriatic acid is run into the still about 2 ft. deep, then gradually manganese

mud is admitted until an even current of chlorine is produced. Finally, to utilize the last of the acid and drive off the dissolved chlorine, steam is blown in. The spent liquor then goes back to the recovery plant.

The reactions which occur in recovery are about as follows:

I. $100MnCl_2+160CaO=100MnO+60CaO+100CaCl_2$.
II. $100MnO+60CaO+86O=48CaO.MnO_2+14MnO.MnO_2+12CaO.2MnO_2$.
III. $48CaO.MnO_2+24MnCl_2=24CaO.2MnO_2+24MnO+24CaCl_2$.
IV. $24MnO+12O=12MnO.MnO_2$.

From $124MnCl_2$ (original 100 and second addition of 24) there are produced $98MnO_2$ (along with 36CaO and 26MnO).

Deacon Process. The Deacon process is based on the oxidation of gaseous hydrochloric acid by the oxygen of the air in the presence of a suitable catalyzer.

$$2HCl+O=H_2O+Cl_2.$$

The catalyzer most used is copper chloride, which functionates as follows:

(1) $2CuCl_2=Cu_2Cl_2+Cl_2$;
(2) $Cu_2Cl_2+O_2=2CuO+Cl_2$;
(3) $2CuO+4HCl=2CuCl_2+2H_2O$.

This reaction begins at 250° C. and reaches its maximum at 400° C. The rate of action of the catalyzer depends upon the surface exposed more than on the amount, and therefore the catalyzer used in practice is broken bricks or burnt clay balls which have been soaked in copper solution (3 per cent) and dried. The reaction is slightly exothermic, but heat must be supplied to make up for the loss by radiation, etc. In practice about 60 per cent of the hydrochloric acid is decomposed, but the rest is recovered as weak acid. The catalyzer soon loses its activity from a variety of causes, principal of which seem to be the presence of sulphuric acid and arsenic in the muriatic acid.

The gases, hydrochloric acid, air and moisture, from the decomposition of salt by sulphuric acid in an ordinary salt cake furnace, are cooled by passing through long glass pipes and a small tower filled with coke to remove moisture. They next pass to an iron preheater, where they are heated to 400° C. (hot, dry hydrochloric acid has little action on iron). The hot gaseous mixture then passes through the decomposer filled with the contact substance, the temperature of which is carefully regulated. The decomposition is here effected, the escaping gases being chlorine, water in the form of steam, hydrochloric acid, nitrogen, and a little oxygen.

The gaseous mixture is first cooled by passing through a long series of pipes. The hydrochloric acid is next removed by washing with water in

a scrubbing tower, and is finally dried by washing with sulphuric acid in a lead-lined tower. The contact substance is removed every two weeks, one-sixth at a time, thus each portion remains in service twelve weeks.

The Deacon process produces chlorine of about 5 to 8 per cent volume concentration. This is its chief drawback. It produces chlorine more cheaply than the Weldon process, but the plant is expensive and there have been few new Deacon installations since the advent of the newer electrolytic processes.

In the Welden process about 35 per cent of the hydrochloric acid is converted to chlorine, the rest to waste calcium chloride. In the Deacon process about 60 per cent is converted and the rest recovered.

Liquid Chlorine. Chlorine can be condensed to a liquid at 15° C. by a pressure of 4 atmospheres, or at atmospheric pressure by a temperature of −34° C. Its specific gravity is 1.43, one volume of liquid corresponding to about 400 volumes of gas.

The liquefaction of chlorine facilitates its transport and use in definite regulated amount as in water purification and organic synthesis.

Chlorine is liquefied commercially either by cooling to a very low temperature, −45° C., or lower without any pressure (Linde process), or by a combination of pressure and cooling (Knietsch or Badische process).

The Badische process has been in successful use in this country for several years. The chlorine to be liquefied must be highly concentrated to insure high per cent liquefaction and free from moisture so that neither the gas nor the liquid will attack the iron apparatus or cylinders. It is compressed by means of a liquid piston operating in a U-shaped apparatus. The metal plunger moves up and down in petroleum in one leg and communicates its motion to concentrated sulphuric acid, in the other arm of the U chlorine is sucked in the acid side on each up stroke and compressed on the down stroke and passes by way of a separator to a condenser where under the influence of low temperature it liquefies and is filled into the shipping containers.

Hypochlorites. Most industrial uses of chlorine depend upon its oxidizing action, particularly in the form of alkali or alkali earth hypochlorite. The hypochlorites also afford an easy means of transport.

Chlorine combines with aqueous solutions of the alkaline and alkaline earth hydrates, or with the hydrates in the presence of moisture-forming hypochlorites.

$$2\,NaOH + Cl_2 = NaOCl + NaCl + H_2O.$$

The hypochlorites are very powerful bleaching and oxidizing agents. Calcium hypochlorite is the cheapest powerful oxidizing agent that we have. Their value depends in most cases upon the ease with which they give up oxygen to oxidizable organic matter, rather than to any direct chlorinating action of the contained chlorine.

$$Ca(OCl)_2 = CaCl_2 + O_2.$$

Aqueous solutions of hypochlorites are produced in large quantities for use at the place of manufacture. Because of their bulk (it is difficult to prepare hypochlorite solutions much over 130 grams hypochlorite per liter) and instability, such solutions are seldom transported. Occasionally bleach liquor (calcium hypochlorite solution) is shipped a few hundred miles in tank cars if it can be used immediately.

Sodium and potassium hypochlorite solutions (Eau de Javelle, Labarraque solution) are made to some extent by the direct action of chlorine gas upon solutions of the respective alkali hydrates for use in laundry work, bleaching and disinfecting. They are more commonly produced from calcium hypochlorite by double decomposition.

$$Ca(OCl)_2 + Na_2CO_3 = 2NaOCl + CaCO_3.$$

Calcium hypochlorite is cheaper and equally good for many purposes. It is made by absorbing chlorine in milk of lime, which takes it up with great avidity. The manufacture is very simple. It is merely necessary to keep the lime in excess throughout and to keep the temperature below 35° C. If the chlorine gets in excess, or the temperature above 37° C., rapid decomposition and formation of chlorate begins. The presence of iron likewise tends to cause decomposition, particularly if there be little excess of lime. In the manufacture of bleach liquor it is preferable to dilute the chlorine with air as the danger of local overheating is thereby greatly reduced. The apparatus in which bleach liquor is made and stored is commonly constructed, or at least lined with Portland cement concrete, which is not acted upon and answers the purpose admirably. Fig. 128 shows a very good type of bleach liquor machine in section. A mixture of lime and water meets a stream of chlorine on the countercurrent principle, is elevated by a centrifugal pump, more lime is added and the operation is repeated till the entire charge is up to the desired strength, the operation being entirely continuous and automatic except as regards the addition of lime.

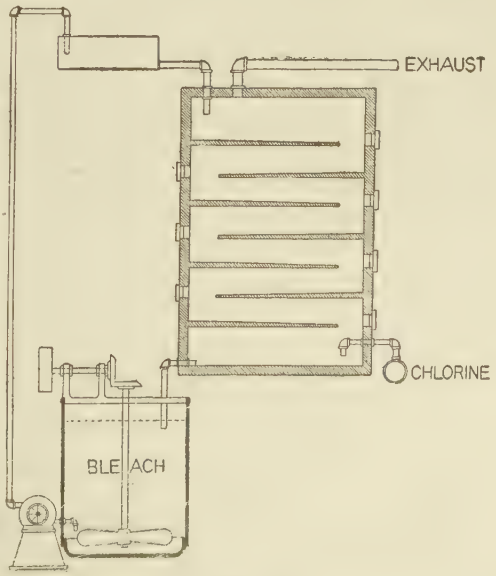

Fig. 128

Although calcium hypochlorite is almost always used in solution, it is commonly manufactured for sale in the solid condition which is more

stable and more easily transported. Slaked lime, $Ca(OH)_2$, containing a slight excess of water (2 to 5 per cent) readily takes up chlorine, forming bleaching powder which has the composition,

$$CaO.CaOCl_2+2H_2O.$$

The CaO in the best bleaching powder amounts to about 10 per cent Bleaching powder is readily soluble in water; the excess lime forming a sediment:

$$2CaOCl_2+H_2O=Ca(OCl)_2+CaCl_2+H_2O.$$

In making bleaching powder burnt lime low in magnesia and carbonic acid is first slaked so as to contain about 26 per cent water. It is then carefully sifted through iron screens and allowed to cool completely. It is then spread in a thin layer 3 or 4 ins. deep on the floor of a so-called "chamber," a room usually about $6\frac{1}{2}$ ft. high. Chlorine gas is then admitted through the roof and slowly passes to another chamber in series after the lime in the first chamber has taken up most of the chlorine. It usually takes about twenty-four hours for the lime to become completely saturated. In case lime deeper than 2 ins. is placed on the floor, it becomes necessary to interrupt the gassing and for workers to enter the chamber and turn the lime with a spade. Finally the bleach is shoveled into wooden casks or iron drums painted with asphalt paint. The chlorine must be fairly dry and must not be admitted too rapidly. The temperature of the chamber is kept below 45° C. Chlorine diluted with air to about 40 per cent by volume works well. With gas less than 30 per cent chlorine, mechanical absorbers or shelf absorbers with very thin layers of lime must be used instead of chambers. The ordinary bleach chambers are constructed of lead, stone or cement, with usually an asphalt floor. They may be quite large, 30 by 100 ft. is a common size, and must be provided with suitable doors, peep holes, etc. Two hundred square feet of chamber floor is necessary for each ton of bleach produced per week.

Potassium Chlorate. If chlorine acts upon milk of lime at a high temperature (60 to 70° C), the chlorine being in excess, hypochlorite is formed only as an intermediate product, which immediately is converted to chlorate, the final reaction being

$$6Ca(OH)_2+12Cl=Ca(ClO_3)_2+5CaCl_2+6H_2O.$$

This is the reaction upon which the manufacture of chlorate is based. Chlorine is systematically passed over milk of lime in cast-iron cylinders provided with stirrers, which are kept at the proper temperature mainly by the heat which the reaction itself evolves, if the combination is allowed to proceed at a sufficiently rapid rate. The chlorine is passed over the surface of the lime water till most of the lime has dissolved and been converted into chlorate. Any unabsorbed chlorine passes to another fresh cylinder in series where it is utilized. The solution is then boiled down to

about 1.35 specific gravity with potassium chloride, which reacts, forming potassium chlorate,

$$Ca(ClO_3)_2 + 2\ KCl = 2\ KClO_3 + CaCl_2.$$

On cooling the bulk of the potassium chlorate crystallizes out. The mother liquors are boiled down a second and third time and strongly cooled to recover the small amount of chlorate which remains in solution. The crude potassium chlorate is purified by recrystallization, and is washed and dried in a centrifugal machine.

Sodium Chlorate. Sodium chlorate is much more soluble than the potassium salt, and cannot be made in quite the same way. In the manufacture of sodium chlorate, calcium chlorate is first made. This is boiled down to about 1.5 gravity and then cooled. Four-fifths of the calcium chloride solidifies. The mother liquor is drained off and most of the calcium precipitated with sodium sulphate, a little sodium carbonate being added to remove the last of the calcium. The solution of sodium chloride and sodium chlorate is then boiled down. Most of the sodium chloride separates from the boiling hot solution and is removed. The solution is then cooled, and much of the sodium chlorate crystallizes out. Twenty per cent or so is, however, left in the mother liquor, which goes back into process. The separation is based on the difference in solubility of sodium chlorate and sodium chloride in hot and cold solutions.

Electrolytic Manufacture of Chlorate. If an alkali chloride solution is electrolyzed and the anode and cathode products allowed to mix as formed, at ordinary temperature alkali hypochochlorites are formed:

$$NaCl = Na + Cl, \quad Na + H_2O = NaOH + H, \quad 2NaOH + Cl_2 = NaOCl + NaCl$$

If the temperature is above 40° C, chlorate is formed:

$$3NaOCl = NaClO_3 + 2NaCl,$$

particularly if the solution is slightly acid. A secondary reaction which occurs is the reduction of chlorate by the hydrogen formed at the cathode.

In actual practice it is customary to electrolyze at a temperature of 70 to 100° C, the heat being produced by using a high current density which also gives a high yield per unit of plant. At this temperature the substances primarily formed at the anode are very destructive to most anode materials. Platinum anodes are least acted upon, and are generally used. The cathode reduction can be largely reduced by the addition of a little calcium hypochlorite to the electrolyte of alkali chloride. This forms a coating of lime on the cathode, and increases the current efficiency greatly.

The destruction of chlorates during electrolysis may also be reduced by maintaining the electrolyte slightly acid, either by the addition of a little hydrochloric acid periodically, or an acid salt, such as potassium bichromate, which at the same time probably forms a film of chromium

oxide on the cathode and reduces the hydrogen reduction. Copper cathodes are generally used.

Gibbs Process. In the Gibbs process, Fig. 129, for the manufacture of potassium chlorate, which has been in very successful operation for a number of years, a solution of potassium chloride containing a little potassium bichromate is passed between anodes of platinum gauze supported on a lead backing, and cathodes of copper in the shape of rods. The distance between anodes and cathodes is only 1–64 inch. The electrodes are kept apart by insulating knobs on the copper rods. The apparatus consists of rectangular wooden frames, alternating with lead plates which support the platinum gauze, packed together in a frame like a filter press, with rubber gaskets between. A great many cells thus occupy only a very little space, the current passing from one cell to the next in series. The rapid mixture of the primary anode and cathode products is brought about by the hydrogen bubbles formed at the cathode and the rapid circulation of the electrolyte. The chloride solution enters the apparatus at about 20° C., it leaves it at about 70° C., carrying about 3 per cent $KClO_3$. It passes to a refrigerator, where the chlorate crystallizes out, and after resaturation with potassium chloride and adjustment of the free acid goes back into process, the entire operation being continuous and practically automatic. The temperature of the cell is controlled by the rate of flow of the electrolyte.

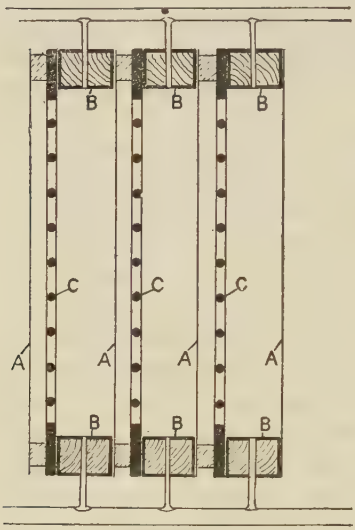

FIG. 129.

Owing to the much greater solubility of sodium chlorate, this process is not suitable for its production. In the production of sodium chlorate an electrolyte of salt and a little calcium hypochlorite is used, and electrolysis is continued until the sodium chlorate has reached a concentration of about 700 grams per liter. The electrolyte is kept saturated with sodium chloride throughout.

Bromine. Bromine is manufactured from the bromides of the alkali and alkali-earth metals. These salts do not occur in nature in quantity in high concentration and are always associated with large quantities of chlorides. The bromides accumulate in the mother liquors from which the chlorides have been extracted. Such mother liquors serve as the chief raw material of the bromine industry.

The principal sources are the mother liquors of various salt wells in the United States (Michigan and Natrona, Pa.), and mother liquors

from the manufacture of Carnallite at Stassfurt, Germany. The Carnallite mother liquors contain about $\frac{8}{10}\%$ bromine in the form of magnesium bromide. The concentration of the American mother liquors is higher and has enabled the American producers to wrest a considerable share of the world's market from their forsign competitors who at one time enjoyed a practical monopoly.

From such mother liquors bromine is liberated either by the action of chlorine or by direct electrolysis. The former method (Process of Dow, etc.), is simpler and probably cheaper and better. It depends upon the simple reaction

$$MgBr_2+Cl_2=MgCl_2+Br_2.$$

The mother liquor containing bromide is caused to meet a stream of chlorine on the counter current principle in a stoneware tower, which may be of the Lunge plate tower type or filled with stoneware balls to increase the surface of contact. The amount of chlorine is regulated so that practically all is used up in the liberation of bromine so that the secondary formation of bromine chloride is minimized. A large part of the liberated bromine remains dissolved in the liquor flowing from the reaction tower. It is collected in granite wells and heated to boiling with live steam which expels the bromine. This is condensed in stoneware worms. The crude bromine contains about 2 to 4 per cent chlorine. The chlorine may be removed by treating with ferrous bromide solution and redistilling, the chlorine being held back as ferrous chloride. The crude bromine may also be purified by being heated very slowly to a point just below the boiling point of bromine and held at this temperature (59° C.) for thirty-six to forty hours.

The electrolytic processes depend upon the fact that bromides decompose at a lower voltage than chlorides and hence are first decomposed. Diaphragm cells are used. Owing to the low concentration and the large bulk of liquid to be handled the efficiency is low.

In the processes depending on displacements by chlorine, the chlorine may be generated within the liquor by the action of muriatic acid on manganese dioxide, but the use of externally generated chlorine is simpler and gives a better control of the process.

Instead of boiling out the bromine from the chlorinated mother liquor with live steam it may be expelled by a current of air and absorbed from the bromine laden air in a solution of pure bromide such as ammonium bromide in which bromine is much more soluble than in a solution carrying large amounts of chlorides (Dow process) and then worked up into commercial bromides. Or bromine may be absorbed from the bromine laden air with a solution of an alkali carbonate or with a solution of ferrous bromide (Schaefer process) which absorbs the bromine, forming ferric bromide, from which the pure bromine is readily recovered in a pure and concentrated form.

Bromine is used in metallurgy (bromo-cyanogen process), in the manufacture of bromides for use in pharmacy and the photographic industries, and also as a disinfectant.

Iodine. The chief sources of iodine are the mother liquors from the refining of Chilean nitrate of soda and the ashes of sea weeds. About 500 tons per annum are produced from the former source and 200 from the latter.

The nitrate mother liquors contain up to about 25 per cent sodium iodate. The iodine is liberated by the addition of sodium sulphite and acid sodium sulphite (from SO_2) in calculated amount.

$$2NaIO_3+3NaSO_3+2NaHSO_3=5Na_2SO_4+I_2+H_2O.$$

The iodine is filtered off and purified by sublimation in cylindrical iron retorts with stoneware receivers, or by distillation with steam.

The ashes of sea weeds contain iodine in the form of sodium iodide. The ashes are lixiviated with water and the iodide separated by fractional crystallization. The iodine is then separated from the iodide solution by the action of chlorine, sometimes generated within the solution by the action of muriatic acid on manganese dioxide

$$2NaI+Cl_2=2NaCl+I_2.$$

Iodine and iodine compounds have very valuable therapeutic properties. Iodine is used in the aniline color industry, in the manufacture of iodoform, and in the production of pure potassium iodide, which is largely used in medicine and photography.

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CHAPTER IX

ELECTROCHEMICAL INDUSTRIES

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By industrial electrochemistry we mean the application of electricity to the manufacture of chemical compounds. The electric current may be utilized in two ways: First, the decomposing effect of a direct current when passed through solutions or molten baths causes a separation of the same into constituents which may be of commercial value as such or else be easily converted into valuable products; second, the current may be used for its heating effect, causing combinations of elements or compounds which cannot be made to take place in ordinary furnaces, or which might suffer contamination if made to take place in such furnaces. We call the first type of operations electrolytic processes and the second type electrothermal processes.

Caustic Soda. By far the most important of the first type of process at the present time is the production of caustic soda from common salt, which has been covered in the previous chapter together with the production of chlorine, hypochlorite, and chlorate.

Pigments. The electrolytic manufacture of pigments has attracted a great deal of attention, but up to the present time has attained no great prominence because of the many unsolved technical difficulties. The production of white lead by the electrolytic dissolution of a lead anode and subsequent precipitation of the basic carbonate has been in commercial use, but is now abandoned. The electrolyte used consisted of a dilute solution of sodium carbonate to which was added a much larger portion of a sodium salt whose acid radicle formed with the lead a soluble compound. Chlorate or nitrate was used for this purpose, it having been found that the use of such a salt in the bath prevented the lead carbonate formed from adhering to the anode and so insulating it. The caustic formed at the cathode of the cell was immediately neutralized by the introduction of a current of carbon dioxide, thus supplying the ingredients used in the process directly as sheet lead anode and gaseous carbon dioxide. The greatest difficulty met with in the commercial operation was the dropping of small pieces of undissolved anode into the deposit of white lead at the bottom of the cell which caused poor color. Another difficulty was the crystalline nature of the deposit at times obtained. More study of the

proper conditions for operating this process must be made to insure its success. Lead chromate can also be obtained in the same manner by using a bath of potassium dichromate and nitrate, regenerating the solution with chromic acid.

The sulphides of cadmium, antimony, etc., have also been made by the use of these metals as anode in a solution of sodium hyposulphite, though the process has never attained much commercial prominence.

Oxygen and Hydrogen. The demands for the gases, oxygen and hydrogen for welding purposes, and hydrogen for the hardening of fats, has within recent years grown very considerably. Where essentially pure gases are demanded on a small scale the electrolytic method of producing them has as yet found no competitor. The fractionating of liquid air for the production of oxygen undoubtedly produces this material at lower cost than the electrolytic process, but its purity rarely exceeds 95 per cent whereas electrolytic oxygen can be obtained with less than .2 per cent of impurity. At the same time in the production of electrolytic oxygen there is obtained hydrogen as a by-product, this hydrogen being readily purified to 99.9 per cent, and at a reasonably low cost if proper credit for oxygen is given.

There have been innumerable cells devised for the production of oxygen and hydrogen in times past, but at the present time development is tending toward what is known as the unit type cell, or rather the cell containing one element of anode and cathode. These cells are essentially steel boxes coated with enamel or protective paint, both inside and outside, and for electrolyte they use a solution of caustic soda. Perforated steel plates form the anode and cathode, a small dependent one being usually connected with the positive terminal of the electric circuit, and a pair surround with an asbestos diaphragm and spaced equidistant from the central plate being connected as a multiple cathode. The two gases, oxygen and hydrogen, are taken off the cell through suitable conductors and led to gas holders. The only attention such cells need is to keep them filled with distilled water at the rate of about 1 gallon per 100 cu.ft. of oxygen produced. The standard type of such electrolyzer produces 7.93 cu.ft. of oxygen per 1000 ampere-hours, and double this quantity of hydrogen. The E.M.F. of the different types of cells varies somewhat with the cell, being approximately 2 to $2\frac{1}{2}$ volts.

Calcium Carbide. When lime and carbon are mixed together in proper proportions and the mixture heated to an extremely high temperature the lime is reduced and the metallic calcium unites with the excess of carbon present to form the carbide, CaC_2. In general the electric arc is used as the source of heat, though resistance systems have been more or less successfully employed. The reaction which takes place in the furnace is:

$$CaO+3C=CaC_2+CO.$$

this reaction would require a mixture of 875 parts by weight of lime to

563 parts of carbon, though in actual practice the proportion of carbon used for the above quantity of lime rises as high as 650 parts, the excess being consumed in other ways than by the above reaction.

The original carbide furnace consisted merely of a basin into which dipped two electrodes between which an arc was sprung, the reacting mixture being fed directly into the arc. The melting-point of the carbide is in the neighborhood of 1800° C., and so the mass sets almost as fast as formed. When the basin was full of set carbide the whole was removed from under the electrodes, allowed to cool and the carbide dug out. The operation was thus an intermittent one, and rather low energy efficiency was attained. A continuous furnace later replaced this primitive type.

Fig. 130 shows one form of this furnace. It consists of a ring mounted on trunnions, so as to revolve in a vertical plane. The whole is made of cast-iron segments bolted together, each piece having its own individual lining of carbon. Hanging down between the two sides is a carbon electrode *C* forming one terminal of the circuit, the other terminal being the carbon lining of the furnace. The mixture of carbon and lime is fed into an arc sprung between the electrode and the furnace walls. As the carbide is formed the furnace is revolved away from the electrode, making space for more product, cover plates *A* being put on as necessary. As the furnace revolves the material inside cools, and by the time it reaches the side opposite the electrode is so cold that the side and cover plates on this side may be removed and the carbide taken out, the side plates again being reassembled at the top. In this way the furnace can be run continuously. Another form of this furnace uses instead of the carbon lining of the furnace for one of the poles another electrode directed towards the first one, between which the arc is sprung and the material fed. The furnace in use at Niagara Falls is of this latter type. It is 8 ft. in diameter, the outer ring being about 24 ins. deep. It revolves once in twenty-four hours. With an energy consumption of 500 horse-power, one furnace will produce 2 tons of carbide per day. Only about 40 per cent of the heat equivalent of this energy is absorbed in the reactions.

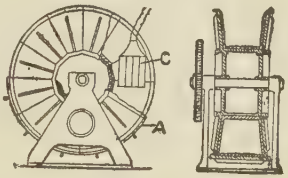

FIG. 130.

Late developments in the carbide industry have brought about the adoption of a multi-phase tapping furnace of considerably larger energy capacity. These furnaces are simply large steel boxes lined with refractory material and are built in capacity up to 20,000 H.P., this latter type using at least six electrodes arranged in two three-phase circuits. Such a furnace shows a very considerable economy in labor over the smaller types in use a few years ago, as well as an increased output per unit of power consumed. With a furnace charge consisting of very pure lime crushed to egg size and a chestnut coke containing 90 per cent fixed carbon, the

charge being proportionately 60 per cent lime and 40 per cent coke, it is not unusual to obtain yields of over 11 lbs. of 85 per cent carbide per horse-power day. In Europe these large furnaces are often built of an enclosed type and the hot gases evolved, consisting largely of CO, are led through flues to points of utilization, such as lime kilns and boiler plants. There seems to be no limit of size in which these furnaces can be built except that imposed by dimensions of available electrodes of suitable quality, of transformers, and of conductors.

Artificial Abrasives. *Alundum.* Of recent years there has been marked increase in the production of artificial abrasives. The most important and the earliest developed of these substitutes was carborundum, which will be described later. This material, however, while extremely hard and possessing excellent cutting powers, is at the same time very brittle and for many purposes has not proven a satisfactory substitute for natural emery. Attempts have, therefore, been made to produce an artificial corundum or crystallized alumina and this industry at the present time is developed on a large scale.

The general principle underlying the production of artificial corundum, which appears on the market under various names, alundum, aloxite, crystolon, etc., is the differential reduction of an aluminum ore. Such ores contain various impurities as silica, oxides of iron, oxides of titanium, etc., and mixed with a reducing agent high in fixed carbon in such proportions as to permit of a reduction of practically all the impurities with only a small amount of the alumina. The whole mass is melted down in a combination arc-resistance type of electric furnace. The furnacing of such a mixture produces a fused mass which separates into layers, the heavier metallic impurities settling to the bottom, upon which floats the mass of fused alumina. In most cases it is not advisable to tap this mass out of the furnace, and smelting is carried on until the hearth of the furnace is filled with the desired product when it is torn down and the fused mass dug out of the cooled hearth, hand picking readily separating the fused alumina from the metallic alloy in the bottom of the hearth.

The production of these materials is quite a complex art in itself, as various proportions of impurities are desired in the unreduced state in the alumina their presence promoting different degrees of hardness or toughness. The character of crystallization is also an important factor in determining physical properties and proper cooling of the fused mass must not be overlooked.

Carborundum. When silica is heated to a very high temperature in contact with an excess of carbon a carbide, SiC, is formed. This is the well-known abrasive called carborundum. The reactions by which it is made may be represented as:

$$SiO_2 + 3\,C = SiC + 2\,CO$$

The arc furnace used in the production of calcium carbide or alundum cannot be employed in the manufacture of carborundum, because of the liability of overheating. Although a high temperature is needed for its formation, if that temperature is exceeded metallic silicon will be volatilized from the formed carborundum and graphite will be left behind. It was this accidental discovery that led to the development of the artificial graphite industry to be described later. In practice the carborundum furnace consists of a bed of firebrick 16 ft. long and 5 ft. wide serving as a permanent foundation. The rest of the furnace structure, as the end and side walls, are laid dry and torn down, and replaced with each run of the furnace. The mixture with which the furnace is charged, 3.5 tons of carbon, 6 tons of sand and 1.5 tons of salt is next shoveled on this foundation, carrying up with it the side walls as necessary for its retention. Through the center of this mixture *M*, in Fig. 131, is placed a core of granulated carbon which serves as the resistor, for the development of the electrical heat in the furnace. The ends of this core are in contact with the permanent end connections *E* consisting of carbon bars between which the copper conductors are laid. Such a furnace takes about 1000 horsepower and runs for 36 hours, at the end of which time 3 to 4 tons of commercial carborundum have been made. After such a run the granulated coke forming the heating core has been graphitized, and immediately surrounding and in contact with it is a layer of graphite produced from overheating the carborundum first formed there. Surrounding this graphite is the crystallized carborundum in a layer a foot or more thick, beyond which is found the reduced and uncrystallized carbide, the partially reduced mixture and finally unaltered mixture. The last three products are usually charged back into the next furnace run, though an attempt has been made to utilize the partially reduced material as a refractory. Fig. 132 shows such a furnace in operation, the carbon monoxide being ignited and burning as it issues between the bricks forming the side walls of the furnace.

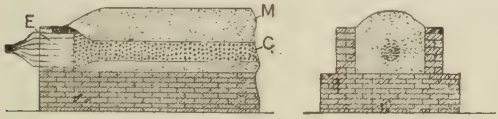

FIG. 131.

Artificial Graphite. The overheating of a carborundum furnace led to the discovery that by suitable decomposition of a carbide graphite is left behind. Heating of pure carbon will not transform it into graphite, it having first to pass through the state of a carbide, which requires that some metal or metallic oxide be mixed with it. In practice, anthracite carrying 8 to 10 per cent ash, uniformly distributed through it, is used for the furnace charge. It may be either moulded into shape first and then graphitized, or else graphitized in powdered form and then used for all purposes of ordinary graphite. It is practically pure, running over 99.5 per cent graphite, all the other impurities having been volatilized at the

temperature of the furnace. Fig. 133 shows the furnace used for graphitizing small carbon electrodes. These small electrodes are packed transversely into the furnace, which bears some resemblance to the carborundum fur-

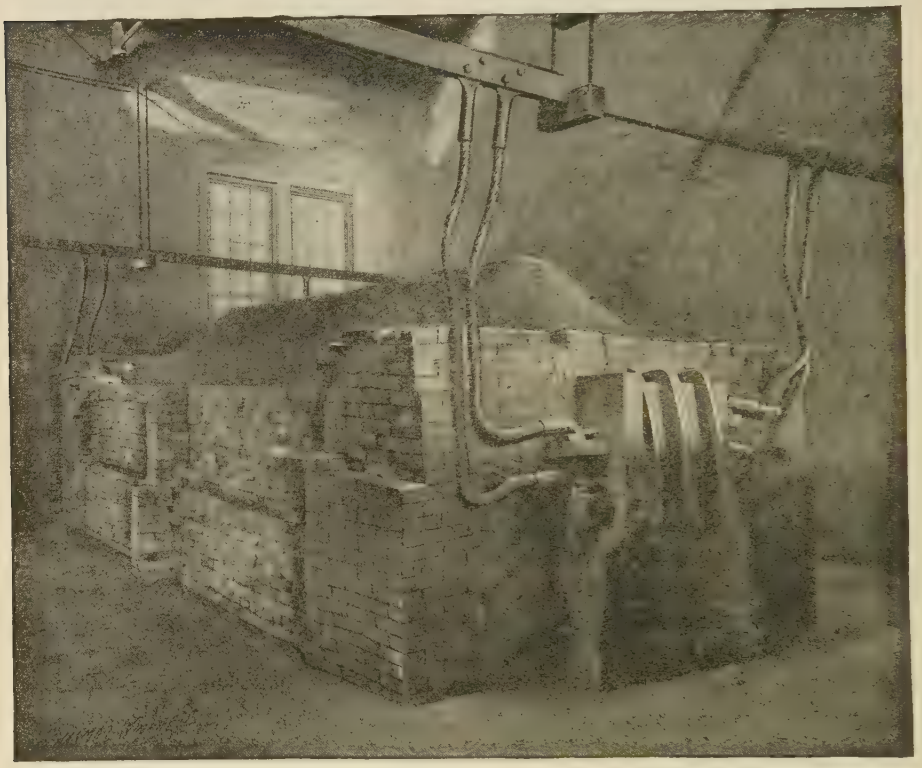

Fig. 132.

nace. Between the piles of electrodes thin layers of granular carbon are inserted and the whole furnace covered over with carborundum residue. The current is led in through the massive electrodes at the end and traverses both the pile of electrodes and the granular packing. The major portion of the heat is generated in the granular portion of the circuit. Such a furnace is 15 ft. long and consumes 1000 horse-power, the run being about 20 hours. Both the carborundum furnace and the graphite furnace are the invention of Mr. E. G. Acheson, of Niagara Falls, N. Y.

Fig. 133.

Ozone. The passage of a current of air through a narrow space between two metallic conductors connected to the terminals of a high tension alternating-current circuit tends to transform the oxygen present into ozone through the medium of the silent electric discharge

taking place through the current of air. This ozone is now rapidly making a field of usefulness for itself in the sterilization of drinking water. A plant for the sterilization of 2700 gallons of water per hour by this system is shown in Fig. 134. This plant uses the Siemens and Halske system of generation, the ozone cells being the two rectangular boxes on the top of the shelf. Each box contains a series of glass tubes lined with tin foil, inside of which is a concentric tube covered with tin foil. Carefully dried air is passed between the two metallic surfaces which are connected with the high-tension circuit.

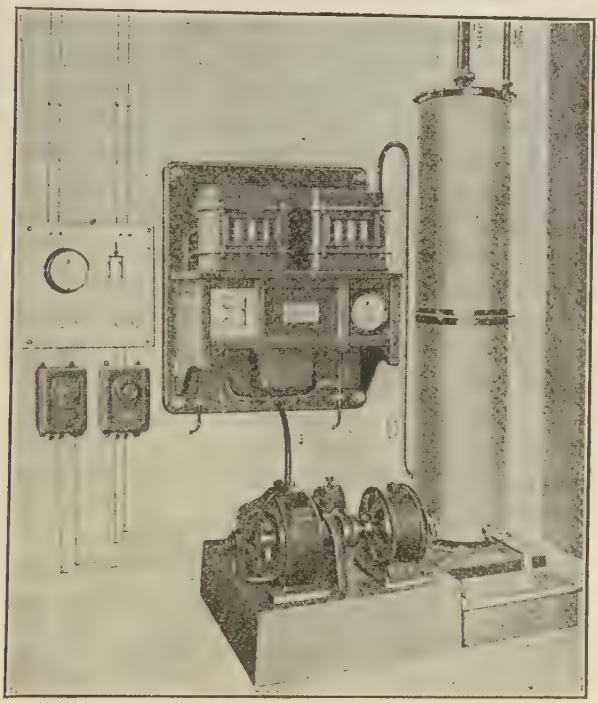

Fig. 134.

The output of a single tube is small, varying from 5 to 50 grams of ozone per kilowatt-hour of energy input. Since only 5 per cent of the energy is efficiently used in chemical reactions, and 95 per cent is transformed into heat to be absorbed in some manner or other, varying with the apparatus, we can see the reason for the small unit.

Numerous inventors are at present turning their attention to the production of ozone in an efficient apparatus capable of working under more adverse conditions of dust and moisture than the present apparatus is capable of doing, for the product is finding a large demand for bleaching paper pulp, wax, oils, flax, etc.

It must not be supposed that the preceding processes represent a

complete list of electrochemical industries. The application of electricity to industrial chemistry is so recent and competition so active that there are many more applications which are in process of development. The changes in this field are so rapid that what appears standard practice to-day may be obsolete to-morrow. The descriptions, however, of the better developed and applied processes will serve at least to give some ideas of the convenience of the electric current in certain lines of work.

Carbon Bisulphide. Practically all the carbon bisulphide used in the United States to-day is made in the electric furnace. This furnace consists of a tall shaft divided by an inside wall into two annular spaces, united below in a common hearth. The inside shaft is kept filled with charcoal and the outside ring with sulphur. Electrodes pass through the hearth walls into the charcoal chamber. The electric heat generated in the furnace warms up the sulphur and charcoal, the sulphur vapors rising up through the hot charcoal and reacting when a zone of suitable temperature is reached. The carbon bisulphide vapors are taken from the top of the furnace through iron pipes and led to suitable condensers. These furnaces are practically automatic in operation; when they get too hot sulphur melts in the outer ring and runs down into the crucible, covering up part of the electrodes, thus increasing the resistance and so lessening the energy consumed in the furnace. The reverse phenomena take place as the furnace cools down below normal.

Phosphorus. Like most electrochemical industries, the production of phosphorus through the assistance of the electric current has reached enormous proportions, without the outside world learning much of the details of operation. No details are available of the furnace used, though the process itself is probably conducted as follows:

Readman Process. Tricalcium phosphate in the form of phosphate rock or bone ash is fused with some form of carbon and silica in a closed electric furnace, the reaction being

$$Ca_3P_2O_8+3SiO_2+5C=3CaSiO_3+P_2+5CO.$$

The phosphorus vapor and carbon monoxide gases are conducted from the top of the furnace through a condenser and deliver liquid phosphorus. The yield of phosphorus is estimated to be about 2 pounds per electrical horse-power-day.

Attention has recently been attracted to the possibility of producing phosphoric acid and its allied compounds by the use of the electric furnace. The fusing of a charge of phosphate rock, silica and carbon in a closed electric furnace, as noted above, produces phosphorus. The yield per unit of power consumed is rather low and the recovery from the charge is not high. The Readman process, as above described, is not suited to the production of cheap phosphoric acid on a large scale, although it is technically possible to produce the acid by an oxidation of the phos-

phorus and recovery in suitable absorption apparatus. However, by suitably changing the proportions of rock, silica and carbon, one can obtain by furnacing this material in a closed type electric furnace, a considerably larger yield of combined phosphorus and phosphoric acid at sufficiently low costs to enable possible competition with other processes. In this process a considerable proportion of the phosphoric acid is displaced by silica, and the charge is cleaned up of the last portions of phosphoric acid which cannot be evolved by direct replacement, by reduction of the phosphoric acid to phosphorus and evolution as such. The gases from the furnace are then oxidized in suitable chambers so that the ultimate product of the furnace is wholly P_2O_5, which is absorbed in water in suitable concentration towers to form phosphoric acid. This may be either changed to ammonium phosphate or be used to make double superphosphate, such as find places in the fertilizer industry. Much experimental work has been done in an attempt to make this process commercial and it affords certain possibilities of successful solution at this stage of development.

Fixation of Nitrogen. *Arc Process.* With the outbreak of the European war certain of the countries were forced to look elsewhere for nitrates than the importation of Chilean nitrate, and they naturally turned to the fixation of atmospheric nitrogen as a solution of their difficulty. It was long known that the passage of a current of air through an electric arc caused a combination of the nitrogen and oxygen to form an oxide of nitrogen, which latter may then be readily converted into nitric acid, or a corresponding nitrate. In Norway this process has been developed on a large scale and is at the present time using about 400,000 H.P. Two types of apparatus are there in use for causing a combination of the nitrogen of the atmosphere with its accompanying oxygen, known respectively as the Birkeland-Eyde furnace and the Schonherr furnace. Developments are wholly toward extending the use of the Birkeland-Eyde furnace because they can be built in units of very large size.

In the Birkeland-Eyde furnace an arc is sprung between special terminals of an alternating current circuit, and spread out into a broad, flat sheet of flame by means of suitable electro-magnets. Through this flat arc is forced a current of air which is rapidly heated to between 2500 and 3000° C. and very rapidly cooled down to below 1500° C. by the peculiar construction of the furnace.

In the arc the oxygen and nitrogen of the air combine to form nitric oxide. The gases leaving the furnace average between 1 and 2 per cent of NO. By a suitable regenerative system the gases are cooled to approximately 1000° C. and thence further cooled by passing through boilers and aluminum coolers until they reach nearly atmospheric temperatures. They are then passed into large, open towers of acid-proof masonry where the NO formed in the arc oxidizes to NO_2 and polymerizes to N_2O_4.

This red gas is then passed into a series of absorption towers operating on a counter-current principle and washed with water or dilute nitric acid, whereby the nitrogen peroxide is further oxidized and absorbed as nitric acid. In such a counter-current system of tower washing 85 to 90 per cent of the combined nitrogen of the furnace gases is absorbed in the form of nitric acid, the final solution of which contains between 30 and 35 per cent of HNO_3. An additional recovery of the nitric gases is obtained by adding to the acid absorption tower system a further series of iron towers washed by soda solutions and in which sodium nitrate and nitrite are produced.

The products of such a plant are dilute nitric acid, nitrate and nitrate of soda, and by further treatment these can be converted into concentrated nitric acid, nitrate of lime, ammonium nitrate and nitrate and nitrite of soda in crystalline form.

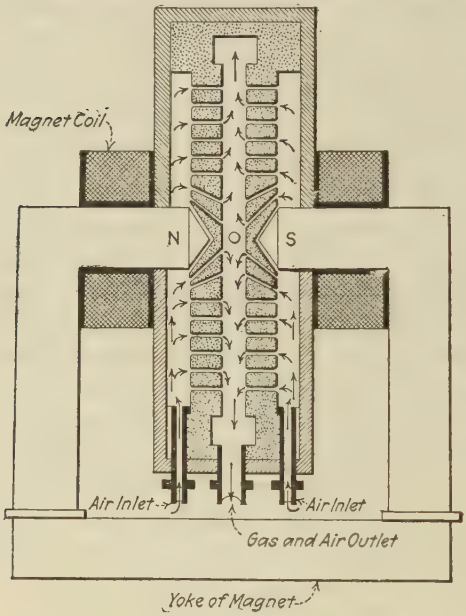

Fig. 135.

In Fig. 135 is shown a sectional view of a Birkeland-Eyde furnace in which *O* is one terminal of the alternating current arc, *N* and *S* poles of the electro magnet. The arc is spread out into a large circular disc in the space between the fire brick sides of the furnace with axis corresponding to the poles of the electro magnet. These sides are perforated for the admission of air across and through the arc.

Fig. 136 is a view of the furnace room of the Birkeland-Eyde plant showing a number of these drum type furnaces in operation.

Fig. 137 is a view of the top of the absorption towers showing the distributing system for insuring proper washing of the gases.

Fig. 138 is a schematic flow sheet of the plant as a whole.

In Germany and Austria-Hungary, in France and in Italy are other arc process plants in operation. These latter plants use what is known as the Pauling system of furnace construction in which the arc is sprung between curved electrodes resembling the horns of a lightning arrester, this arc being rapidly blown out by a high pressure air jet directed upwards between the gap of the horn. Systems similar to those in Norway for handling the gases produced are in use.

The arc processes consume about 13 H.P. years, or more, per ton of nitrogen fixed in the form of dilute nitric acid. The labor required is considerable and the plant investment cost is high. As a result these proc-

esses have so far only found commercial development where water power and labor are comparatively cheap. No commercial installation at the present time exists in the North American Continent, but several small

Fig. 136.

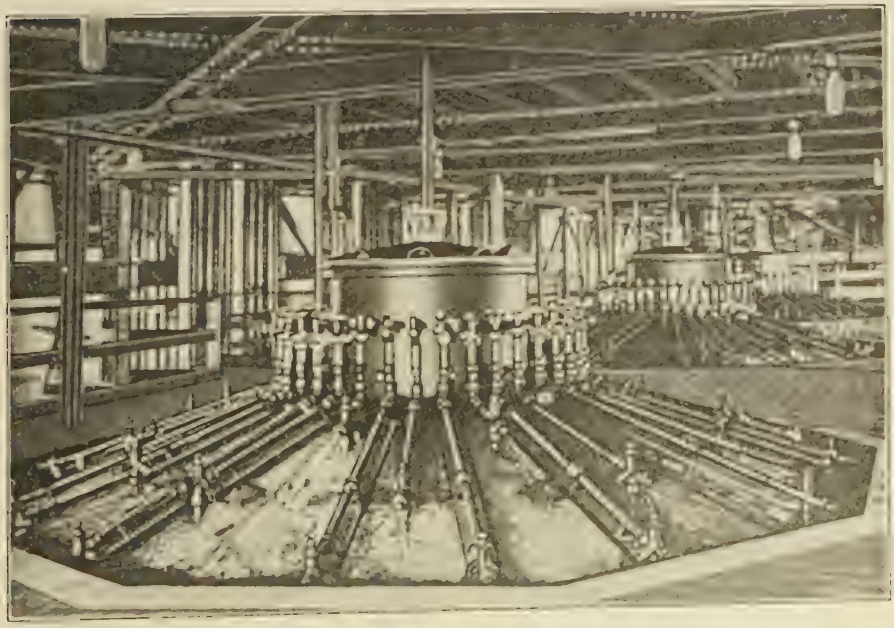

Fig. 137.

experimental plants have been operated for short periods of time; as a matter of record the first serious attempt to develop this process was made at Niagara Falls by Bradley and Lovejoy in 1902–3.

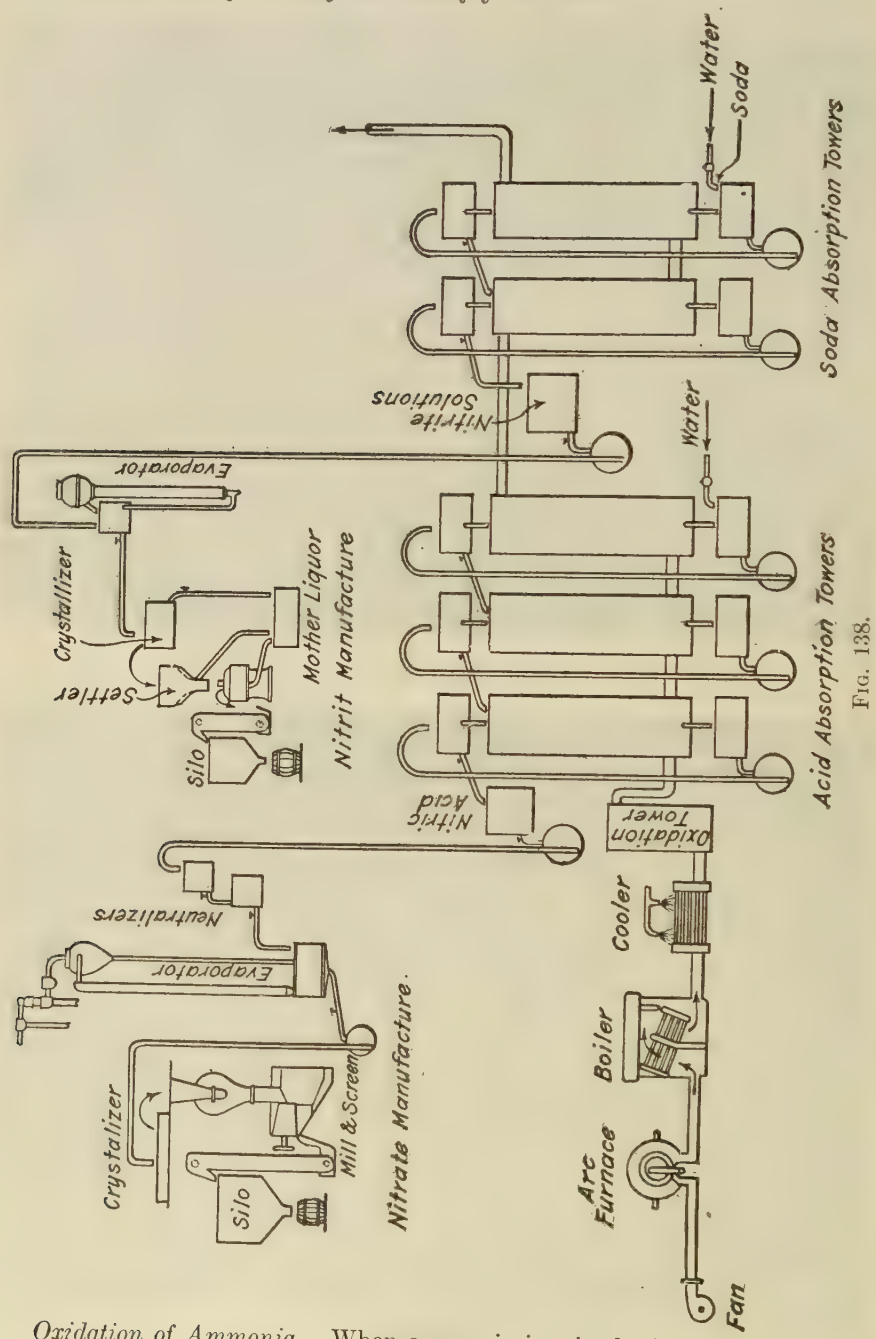

FIG. 138.

Oxidation of Ammonia. When ammonia is mixed with air and passed over a heated platinum catalyzer under proper conditions of mixing, tem-

perature, and rate of flow the ammonia burns to nitric oxide and water vapor. This nitric oxide can then be transformed into nitric acid or nitrates by the same methods of manufacture as are used in handling the gases from the electric furnace in the arc process.

Two systems of carrying out the process of oxidizing ammonia have been developed on a very large scale, Germany in particular depending for most of her nitric acid supply during the war upon the oxidation of ammonia. The older of the processes is known as the Ostwald process. In this process ammonia and air are mixed together in such proportions as to have available an excess of oxygen after all the nitrogen of the ammonia has been converted into nitric acid. This mixture is too dilute to burn of itself or to furnish sufficient heat to maintain the catalyzer at the desired temperature of about 700° C. Consequently, the inventor resorted to the preheating of the mixture of ammonia and air to about 350° C. before passing it through the catalyzer. The catalyzer itself has consisted of various forms of platinum in the shape of platinized asbestos, spongy platinum, fluted and corrugated sheets of platinum, perforated plates, etc. Combustion takes place on the surface of the catalyzer, producing a considerable amount of heat thereby, and the gases are led to coolers, condensers and absorption towers.

The Ostwald apparatus is very simple, consisting of a fire clay tube or envelope, inside of which is placed a nickel tube. The catalyzer is placed over the one end of the nickel tube. The ammonia-air mixture passes upwards between the clay tube and the nickel tube and becomes preheated by a counter-current system to such degree as is necessary to insure the maintenance of proper temperature on the catalyzer. After passing through the catalyzer the heated gases are conveyed downward inside the nickel tube and are cooled off in preheating the mass of oncoming ammonia and air surrounding the tube itself. Efficiencies of oxidation of ammonia above 90 per cent are claimed for some of the later modifications of this process, but the usual Ostwald apparatus rarely attains above 80 per cent. One reason for this loss of efficiency is due to the fact that on preheating ammonia it decomposes into its elements before striking the catalyzer.

A second system of oxidation has been developed in which ammonia is mixed with air in the proportions of approximately one volume of ammonia gas to ten volumes of air, and the mixture passed through a very fine mesh platinum gauze screen. As above noted, the combination in air will not take place because the heat generated in the reaction is not sufficient to maintain the catalyzer at the required temperature. In this last-named process heat is supplied to the catalyzer by connecting it as a resister in an electric circuit. The consumption of electrical energy is very small and with reasonable power costs is fully offset by the decreased investment in equipment and the much higher efficiency obtained in the oxidation of ammonia, which over long series of tests has been found to

be as high as 95 per cent and even above. In this latter process it has been found advantageous to screen the oncoming current of ammonia-air mixture from the radiated heat of the catalyzer by interposing a cellular or other type of cooler.

The gases from the oxidation towers are much more concentrated in nitric oxide than those from the arc furnace, and as a consequence require very much smaller coolers and absorption tower space for their conversion into nitric acid. Developments in the oxidation of ammonia and in the absorption of the concentrated gases have been very rapid within the past two or three years and the processes are now upon a firmly established basis abroad and undoubtedly will be in operation in this country in the near future as they show themselves quite capable of producing nitric acid much more cheaply than it can be made from Chilian nitrate.

Cyanamid. Nitrogen is absorbed by hot calcium carbide, forming what is known in the trade as *Cyanamid.* The reaction involved in the absorption is a reversible one, reading as follows:

$$CaC_2 + N_2 \rightleftarrows CaCN_2 + C.$$

This industry is making rapid strides, there being some fourteen plants in operation throughout the world prior to the war, the bulk of the product being consumed in the fertilizer industry.

Calcium carbide is first made from lime and carbon by the usual electric furnace process. This carbide is then finely ground and the powdered material charged into a special form of electric furnace where it is kept at 1000° C. Pure dry nitrogen, produced by the copper or the Linde process, is then passed over the hot carbide and is there absorbed. Starting with a carbide containing 75 to 80 per cent calcium carbide, from 80 to 90 per cent of the theoretical amount of nitrogen will be absorbed, the resulting product being a grayish-black mass of cyanamid, carbide and lime. It contains on the average 20 per cent nitrogen.

The American fertilizer manufacturers require that the material be freed from undecomposed carbide and free caustic lime before they can use it. The product is therefore hydrated in specially designed rotary mixing apparatus before appearing upon the market. A small quantity of mineral oil is added to assist in keeping down the dust. This hydrated, oiled material is sold in the United States under the name *cyanamid.*

If cyanamid is treated with superheated steam its nitrogen content is quantitatively evolved as ammonia, according to the reaction:

$$CaCN_2 + 3\ H_2O = CaCO_3 + 2\ NH_3.$$

Several large installations for the conversion of cyanamid into ammonia are in operation in the United States, the ammonia being transformed into various salts of high purity at the respective autoclave plants.

The oxidation of ammonia to nitric acid is an accomplished fact, the development having received an enormous impetus since the out-

break of the European war. The Central Powers are practically dependent upon the oxidation of ammonia as a source of nitric acid and the cyanamid process and the Haber process are furnishing the bulk of ammonia to these oxidation plants.

When treated with warm water dicyandiamid is formed:

$$2\,CaCN_2+4\,H_2O=2\,Ca(OH)_2+(CNNH_2)_2.$$

A solution of calcium cyanamid when treated with excess of mineral acid forms urea, which can be recovered in largely purified form by evaporation and crystallization.

When fused with common salt sodium cyanide is formed. All of these derivatives are becoming of greater importance as a consumer of cyanamid each year.

Haber Process. The synthesis of ammonia from its elements, nitrogen and hydrogen, has been a commercial accomplishment since 1913 in Germany. The present process was developed from the work of Professor Haber in which he found that by mixing very pure nitrogen and hydrogen in the volume-proportions of 1 : 3 and passing the mixture under an extremely high pressure through a catalyzer electrically heated to about 550° C. they combined to form ammonia. The process is hardly an electrochemical one as only a comparatively small amount of electrical energy for heating the catalyzer enters into the Haber process, in addition to which there is a considerable mechanical energy requirement for compression, etc. Nitrogen used in the process is prepared by fractionating liquid air. The hydrogen is produced either by the Linde-Frank-Caro process of fractionating blue water gas, or by a special water gas process combined with chemical purification. Both gases must be extremely pure. The mixture in the proper proportions is then compressed to 150 atmospheres and passed through a catalyzer operated at the temperature above referred to. This catalyzer has taken on varied forms and is made of varied materials, iron, uranium, manganese, etc., all having been used with considerable success. The gases leave the catalyzing element with about 10 per cent of their volume combined to ammonia and are cooled and the liquid ammonia condensed out or absorbed as desired. The process itself, while using smaller quantities of power than either the arc or the cyanamid process uses much larger quantities of skilled labor and complicated machinery, and up to the present time, while highly developed in Germany, has not found a place outside of that country.

Aluminum Nitride. Within recent years a new carrier of nitrogen has attracted a great deal of attention. If alumina is heated with carbon in the presence of nitrogen to about 1900° C., AlN is formed. This nitride when heated in an autoclave with caustic soda forms sodium aluminate and ammonia, serving both as a means of obtaining a pure alumina for the aluminum industry and for the fixation of nitrogen. Unfortunately the difficulty of obtaining furnaces of the required life are so great as to

preclude any present successful solution of this process of fixing nitrogen, though much effort and money is being expended in the attempt.

Miscellaneous Processes. There have recently sprung up a number of other processes for the fixation of atmospheric nitrogen, all of them more or less related either to the old barium cyanide process or the cyanamid process. The principle of operation is essentially that of passing nitrogen or nitrogen-bearing gases into intimate contact with alkali or alkaline earth metals, either with or without the addition of some form of carbon. The products formed are either nitrides or cyanides of the metal used, and while all are receiving very considerable study, none of them has yet reached a state of even fair-sized commercial operation. They seem to offer possibilities for the production of high-priced nitrogen compounds such as cyanides, etc., but it is questionable if they will find a place in the greatest field of nitrogen consumption—the fertilizer industry.

Iron and Steel. This industry probably represents the largest present development of the electrometallurgical industries. It is treated in more detail in the chapter on " The Metallurgy of Iron and Steel."

The attempt to prepare pure iron by the electrolysis of a ferrous sulphate or ammonium ferrous sulphate solution, in a manner similar to that used in the electrolytic refining of copper, has not met with commercial success. High-grade iron and steel can be made so cheaply by the electrothermic processes that an electrolytic process offers little chance of commercial success.

Ferro Alloys. Probably the largest single development in the electrometallurgical industry at the present time lies in the field of the production of ferro alloys. The European war has forced American manufacturers to enter this industry, and developments have consequently been extremely rapid.

Ferro-silicon is made by charging into a simple electric furnace with open top, a mixture of coke and silicious iron ore, the iron content depending upon the grade of material to be made. The product is tapped out into sand beds and broken up for market.

A similar furnace to that used in the carbide industry charged with a mixture of approximately 60 per cent pure silica rock and 40 per cent coke yields a product containing nearly 95 per cent silicon. This metal is finding a new place in the manufacture of chemically resistant castings.

Ferro-chrome, ferro-manganese and ferro-titanium are similarly made by using chrome, manganese and titanium ores in similar furnaces. In all cases the reducing agent is some form of fixed carbon, usually a high-grade coke. Impurities are slagged off by use of suitable fluxes.

Aluminium. It has not proven commercially possible to reduce the oxide of aluminium, Al_2O_3, by heating with carbon. Instead of the metal a carbide is formed. Electrolysis of the oxide dissolved in a melted bath of the double fluoride of aluminium and sodium to which some

calcium fluoride is added is used universally in the extraction of this metal. Aluminium as demanded by the trade must be of a high degree of purity, and as the usual impurities, silicon, titanium, and iron are less readily oxidizable than the aluminium itself the usual furnace methods of purification by oxidation are not applicable in the case of this metal. Instead the bath and everything entering into it must be most carefully freed of all foreign elements, so that the metal as extracted will meet the exacting demands of the trade.

The chief source of alumina is bauxite, analyzing

	France.	Arkansas.
Al_2O_3	75.0%	55.59%
SiO_2	1.0	10.13
Fe_2O_3	12.0	6.08
H_2O	12.0	28.99

Three processes may be used for the extraction of the pure alumina from this raw material.

(1) *Fusion Process.* Bauxite is fused in a reverberatory furnace with sodium carbonate forming sodium aluminate. The fused mass is leached with hot water, filtered, the alumina precipitated from the filtrate by carbon dioxide and dried for use in the electrolytic pots.

(2) *Bayer Process.* Finely-ground and lightly-calcined bauxite is agitated with a strong solution of caustic soda in a closed vessel under steam pressure. The alumina passes into solution as sodium aluminate and the impurities remain insoluble. The filtered solution is run off into tall cylindrical vessels provided with stirring apparatus, a small amount of freshly-precipitated alumina is added and the whole stirred. In thirty hours about 70 per cent of the alumina in solution will have precipitated itself by hydrolysis, the caustic solution being regenerated and ready for use again.

(3) *Hall Process.* Bauxite is fused in an electric furnace with just sufficient carbon to insure reduction of the impurities, silica, titanic acid and ferric oxide. The alumina is not affected. By repeating this operation the product obtained is pure enough for many grades of aluminium.

The fused bath used for dissolving the alumina was originally cryolite, Na_3AlF_6. This has later been modified by the addition of other salts designed to reduce its melting-point and make it lighter in weight. A typical bath consists of $2AlF_3 \cdot 6NaF \cdot 3CaF_2$, though details of the bath composition are kept secret in many plants.

The vessels used for containing the fused bath are rectangular iron boxes 8 ft. long, 4 ft. wide, and about 2 ft. deep, made of sheet steel stiffened by angles. The inside is filled with a baked mixture of tar and carbon from which a cavity is scooped out in the middle for holding the actual fused bath. Above is suspended four rows of ten each carbon electrodes, 3 ins. in diameter, fastened into rods. These electrodes

slide up and down, being held to the positive current terminal by screw clamps over the rods. A recent modification of the cell involves the use of fewer and larger electrodes.

The bath is fused in the cavity and alumina stirred in. The dissolved alumina is decomposed by the electric current, melted aluminium being plated out on the bottom of the cavity from which it can be tapped as desired. Oxygen appears at the carbon anodes suspended above and consumes part of the carbon to carbon monoxide. The fused fluoride bath itself is not decomposed as long as alumina is added as the bath becomes exhausted.

Such a pot is supplied with 10,000 amperes of current, the resistance offered to the passage of the current serving to supply all the heat necessary to keep it melted. As long as alumina is present in the bath the E.M.F. across the cell varies between 7.5 and 8 volts; as soon as the alumina is exhausted the voltage across the cell rises to 16–20 volts, this rise in voltage being made to actuate a warning signal that the pot needs more alumina stirred into the bath.

Calcium. Calcium is produced by the electrolysis of a fused calcium chloride bath. The calcium is plated out in the solid state and withdrawn from the bath in the form of a rod as fast as isolated.

Magnesium. Quite recently there has been produced in this country the element magnesium in large quantities. The processes have been maintained rather closely guarded but they essentially consist in electrolyzing molten magnesium chloride mixed with various other chlorides to reduce the melting-point of the bath, and in that respect resembling the calcium process.

Sodium and Potassium. These metals are produced by the electrolysis of a fused caustic bath of the corresponding metal. The melted hydrates have great solvent power for the metals and therefore it is necessary to perform the electrolysis within 20° of the melting-point of the hydrates, if a satisfactory current efficiency is to be attained. In the production of sodium the current efficiency is rarely above 45 per cent. The cathode products are chemically equivalent parts of sodium and hydrogen so that as best only 50 per cent of the current is producing sodium, and obvious losses reduce the actual current efficiency to the 45 per cent. The metal is liberated at the cathode, floats to the surface of the bath, and is there drawn off through a trap.

Many attempts have been made to produce sodium electrolytically from a bath of fused chloride, thus eliminating the double electrolytic operations of first preparing the caustic and afterwards again electrolyzing this caustic. Electrolysis of a chloride fusion produces only sodium at the cathode, affording a much higher efficiency of current used. The high melting-point of the chloride has been a very discouraging factor in this electrolysis, as this melting-point is close to the boiling-point of sodium and yields have been low in most cases. Recently the Virginia

Electrolytic Company, working under the patents of Von Kugelgen and Seward have succeeded in carrying out this electrolysis successfully on a commercial scale. They lower the melting-point of the bath very considerably by using a mixture of the chlorides and fluorides of sodium with barium chloride, or mixtures of the chlorides of the alkalies. The cell is constructed of refractory material with a cooled ring cathode near the upper level of the bath. The space above the bath is enclosed air-tight to prevent oxidation of the metallic sodium which collects around the cathode ring at the top and is drawn off from time to time. But little detail has been given out for publication regarding the process, but there seems to be no doubt of its successful solution.

Electrolytic Refining of Impure Metals. *Copper.* Copper as produced by the Bessemerizing of copper matte contains a number of deleterious foreign substances together with silver and gold. Among these substances may be enumerated: Cu_2S, Cu_2O, Au, Ag, Pt, Fe, Ni, Co, As, As_2O_3, Sb, Sb_2O_3, Bi, Bi_2O_3, Se, Te. For economical reasons, it is advisable to separate the precious metals from the copper as the electrical industry requires copper of almost absolute purity, hence some means of refining copper to remove these substances must be used. The most effective means is by electrolytic refining. The crude copper is given a partial refining in a furnace and is then cast into thin flat plates or *anodes* for the electrolytic treatment. These plates are suspended in a bath of copper sulphate and sulphuric acid and a direct current passed from the crude metal plates to others called *cathodes* (see later). Under this treatment the impurities in the anodes behave as follows:

Cu_2S and Cu_2O drop to the bottom as the copper is dissolved out around them and slowly pass into solution. As and As_2O_3 partly dissolve through the action of the current and partly drop to the bottom, slowly passing into solution. Sb and Sb_2O_3 partly pass into solution and partly into insoluble basic salts. Bi and Bi_2O_3 pass into solution and are precipitated out as basic salts. Au, Ag, Pt, Se, Te are not dissolved by the current and drop to the bottom of the tanks as a mud or slime. Fe, Ni and Co pass into solution and are not plated out if copper is present in the solution. Arsenic is not plated out as long as the solution contains free sulphuric acid. In this way we get nothing but copper plated out on the cathode, the impurities either collecting in the slime at the bottom of the tank or in the solution; it is necessary to remove and purify the electrolyte at intervals.

In practice the electrolytes used contain from 10–15 per cent copper sulphate and 5–15 per cent sulphuric acid. Since one ampere of current flowing from an anode to a cathode only plates out or dissolves one ounce of copper in a day and it is not possible with the above electrolytes to use a current density of over 15–20 amperes per square foot of cathode surface without danger of forming rough plating and consequent danger of short circuits, we can readily see that a refinery of any great output

must use enormous electrode surfaces. This has led to the development of two systems of connecting the plates up in the electrolytic tanks, the *series* and the *multiple*.

FIG. 139.

In the series system, Fig. 139, a number of copper anodes are suspended in the bath about $\frac{1}{2}$ to $\frac{3}{4}$ in. apart, only the two end ones being connected with the source of current as shown. The current dissolves copper from the first plate and deposits it on the near side of the next plate; the other side of second plate is dissolved and plated out on the near side of the third plate and so on through the tank. When the anode is nearly consumed it is mechanically separated from the deposit of pure copper on its back. This system is not in very general use, although the largest refinery in the world is equipped with it.

FIG. 140.

In the multiple system, Fig. 140, the anodes and cathodes are arranged alternately, all the anodes being connected to the positive source of current and the cathodes to the negative. The cathodes are thin sheets of electrically precipitated copper made in special tanks by plating copper on greased lead plates from which it is stripped by hand.

Lead. Lead is refined by suspending the impure lead as anode in a bath consisting of 18–20 per cent lead fluo-silicate and 8 per cent fluo-silicic acid to which a little gelatine or glue has been added. Lead, zinc, nickel, and iron go into solution and lead and tin only plate out if the solution is kept pure. The impurities for the most part remain as a sponge sticking to the anode.

Silver. For alloys containing above 90 per cent silver with small amounts of copper and gold the electrolyte used is a solution of 2–4 per cent copper nitrate in 1 per cent nitric acid. Silver and copper pass into solution under the influence of the electric current and silver alone is deposited with the low current density of 18 amperes per square foot employed in practice. The gold settles out as a mud in the bottom of the tanks. On account of the silver precipitating on the cathode as loose crystals mechanical means must be taken to prevent crystal-growths from short-circuiting the cell.

Gold. For alloys very high in gold and containing but small amounts of silver and platinum the electrolyte used is a solution of auric chloride in hydrochloric acid. Gold dissolves and is plated out on the cathode, while the silver and platinum remain behind in the slimes.

Nickel and Bismuth. These metals are at present being electrolytically refined by suspending the impure metals as anodes in chloride baths. No details of the processes are available.

Electroplating. A branch of electrochemistry that has attained enormous commercial importance, yet as regards conduct more nearly resembles the chemical manipulation of the alchemists, is that of coating the surface of one metal with a thin skin of another either for decorative or preservative purposes. Thus base metal is coated with gold for decorative purposes, iron with nickel for preservative reasons. Practically all of this metal coating is now done by suspending the object to be plated as cathode in a suitable bath and electrolytically depositing a coating of the desired metal on its surface. It is not possible here to thoroughly cover all the methods and solutions used in this work, as each establishment seems to cherish its own secret manipulation, a great deal of which secrecy is more imaginative than real.

To insure uniform results the base metal to be plated should be sound, free from pores and sand holes, and above all clean. Cleaning is done by the use of brushes, buffing wheels, acid and alkali baths, the objects to be plated not being touched by greasy hands.

The composition of the baths used are as varied as the establishments, each seemingly possessing its own special formula for each bath. Chemically the baths are as far as possible so constituted that metal is not deposited by simple chemical replacement as such coatings are usually not strongly adherent. A general idea of the baths used may be gained from the following:

Copper. A solution containing 10–12 per cent copper sulphate and 2–3 per cent sulphuric acid. For plating on iron this solution, because of chemical replacement, does not give a particularly good adhering coat and recourse is had to first plating a very thin coating of copper on the iron from a copper cyanide solution, the object being finished in the acid bath, for the reason that regeneration of the cyanide bath by the use of a copper anode is not particularly successful. Such a cyanide bath may be prepared by dissolving a mixture of one part of carbonate of copper and three parts of potassium cyanide in twenty-five parts of water.

Silver. A fairly strong solution of the double cyanide of silver and potassium is most frequently used in plating this metal.

Gold. A similar solution of the double cyanide of gold and potassium is used.

Zinc. But little electroplating of zinc is done at the present time, the simple galvanizing processes being cheaper. Where it is desired to plate zinc without heating the base metal electroplating finds application. The solution used is that of the neutral zinc sulphate to which is added various organic agents as glue, dextrine, etc., in small amounts. These addition agents yield a plating of finer grain and much less crystalline than is produced by the same baths not containing them.

Nickel. A saturated solution of the double sulphate of nickel and ammonia is largely used for nickel plating. As nickel anodes do not dissolve in sufficient quantity to recuperate this bath, nickel sulphate is added from time to time to maintain its saturated state.

Brass. A mixture of cyanides of copper and zinc containing varying proportions of the two metals, depending on the color of the plating desired, will yield a plating of brass. Great skill is needed to use such a bath and much secrecy is maintained regarding the exact composition of a successful brass bath.

The actual conformation of a bath to a definite chemical composition is not of great importance. Using pure salts, keeping the bath free from both dissolved and suspended impurities and of a fair degree of saturation will produce good results over a wide range of compositions. High current densities tend to produce coarse crystalline metals, so that voltage and current regulation of the bath must be given close attention.

After withdrawal from the bath the plated object is well washed with water, or even alkali if an acid bath has been used. Dull or matte finishes are given a plated object by the use of a wire or scratch brush. Polishing is done with rouge, whiting or other polishing powder on a cloth or leather wheel. This mechanical manipulation after plating in many cases plays a more important part in obtaining a desirable ornamental finish than the actual plating bath itself.

Organic Compounds. A broad general view of electrolysis would consider an anode dipped into an electrolyte as a perducing agent, each 96,540 coulombs of electricity passing through it causing the perduction of one gram-equivalent of a substance one unit of valence. A cathode is similarly a reducing agent, the passage of the above quantity of electricity causing a reduction of one gram equivalent one unit in valence. We have here an ideal means of perduction (reduction) in that no foreign materials not essential to the reaction need be added to cause such change as desired and have no contamination of the resulting products to fear. Electrochemical perductions or reductions resolve themselves into a choice of suitable electrode materials, current densities and separation of the effects of anode and cathode through diaphragms. In the field of organic chemistry many applications have been made of electricity to the reactions of perduction and reduction, where conditions are suitable to their use, but strange to say not many on a commercial scale. A few of the prominent commercial processes are the following:

Chloroform. A solution of 20 per cent chloride of sodium to which acetone is added evolves chloroform on the passage of an electric current. The chloroform vapors are removed from the closed cell and condensed. The use of chlorine produced in the caustic soda industry for this purpose is of much greater technical importance than the above direct process.

Iodoform. A solution of iodide of potassium to which alcohol or acetone is added, and the whole electrolyzed, yields a solution of iodoform, which can be crystallized out by cooling. This process is the basis of an important manufacturing industry at this time, and has largely supplanted the old chemical process.

It is impossible to describe here the numerous processes proposed

and in use for electrolytic oxidations and reductions of organic compounds. A few have found commercial application, but most of them are still in the laboratory stage. Reference to the bibliography will serve to inform the reader of the wide extent of application of electrochemistry to the organic division.

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CHAPTER X

LIME, CEMENT AND PLASTER

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Mortar materials may be classified according to their properties, methods of manufacture and materials from which they are made, as follows:

Common Limes are made by burning relatively pure limestone. When mixed with water they slake and show no hydraulic properties.

Hydraulic Limes are made by burning impure limestone at low temperatures. They slake with water, but show hydraulic properties.

Natural Cements are made by burning impure limestones at a low temperature (insufficient to vitrify). They do not slake with water, but require to be ground in order to convert them into a hydraulic cement.

Portland Cement is made by heating to incipient vitrification an intimate mixture of argillaceous and calcareous substances, which product does not slake with water, but upon grinding forms an energetic hydraulic cement.

Puzzolan Cements are formed by incorporating slaked lime with finely ground slag or volcanic ash or by incorporating Portland cement clinker with suitably treated slag and grinding intimately the mixture.

Plasters are made by heating gypsum sufficiently to drive off three-fourths or all of the combined water, which it contains, and grinding finely the dehydrated residue.

The diagram on the following page will explain the above classifications, while Tables I and III show the composition of these various materials.

TABLE I.—ANALYSIS OF VARIOUS MORTAR MATERIALS[1]

Material.	From.	SiO_2	Fe_2O_4	Al_2O_3	CaO	MgO	SO_3	CO_2	H_2O
Lime	Glencoe, Mo.	0.15	0.85		98.01	0.45	....	0.55	....
Lime	York, Pa.	0.52	0.24		97.14	1.28	....	0.96	....
Lime	McNeil, Tex.	0.25	0.15		97.46	0.73	....	1.41	....
Lime	Tiffin, Ohio.	1.61	0.17		57.44	40.36	....	0.41	....
Hydrated lime	Union Bridge, Md.	0.38	0.08	0.06	72.59	0.74	....	2.10	23.11
Hydrated lime	Carey, Ohio.	0.34	0.18		45.37	31.20	....	3.02	20.07
Hydraulic lime	La Farge Cement.	31.10	2.15	4.43	58.38	1.09	0.60	1.28	....
Hydraulic lime	Tiel, France.	19.05	0.55	1.60	65.10	0.65	0.30	....	12.45
Plaster of Paris	Nova Scotia.	0.11	0.01	0.03	38.90	0.14	54.81	0.54	5.33
Plaster of Paris	Buffalo, N. Y.	2.48	0.32	0.40	37.81	0.39	53.12	0.61	4.98
Natural cement	Cumberand, Md.	29.92	4.78	11.23	36.50	11.93	....	5.42	....
Natural cement	Rosendale, N. Y.	27.75	4.28	5.50	35.61	21.18	0.50	4.05	....

[1] From Meade's "Portland Cement."

DIAGRAM OF LIMES AND CEMENTS.

Raw Materials.	Heat Treatment.	Mechanical Treatment.	Properties.	Classification.
Made from relatively pure limestones.	Burned at low temperatures. 600°–900° C.	Slake on addition of water to burned product.	Not hydraulic.	1. Common limes
Made from argillaceous or impure limestone.				2. Hydraulic limes.
				3. Natural Roman or Rosendale cement.
Made from an intimate mixture of argillaceous and calcareous substances in proper proportions.	Burned at high temperatures. 600°–1200° C.	Do not slake on addition of water, but must be ground finely for use.	Hydraulic.	4. Portland cement.
Made from mixtures of slaked lime and blast-furnace slag or volcanic ash.	Not burned.			5. Slag or puzzolan cements.
Made from gypsum.	Burned at from 165°–200° C.		Not hydraulic	6. Plasters.

TABLE II—ANALYSIS OF MATERIALS USED FOR MANUFACTURE OF LIME AND CEMENT

Material.	From	SiO_2.	Fe_2O_3, Al_2O_3.	CaO.	MgO.	CO_2.	SO_3.	Used for
Limestone...	Annville, Pa.....	0.36	0.45	54.45	0.54	43.24		Portland Cement
Limestone...	Glens Falls, N. Y.	3.30	1.30	52.15	1.58	40.98		"
Limestone...	Mitchell, Ind.....	0.74	0.13	52.94	1.87	43.68		
Marl.....	Bronson, Mich...	1.78	1.21	49.55	1.30	40.35		"
Cement Rock	Nazareth, Pa....	13.44	6.60	41.84	1.94	32 .94		"
Cement Rock	Martin's Creek, Pa	11.11	6.31	42.51	2.89	36.57		
Clay.....	Alpena, Mich....	61.09	26.97	2.51	0.65	.....	1.42	"
Clay.....	Suisun, Cal.....	58.44	26.50	1.70	1.88	.....		"
Cement Rock	Rondout, N. Y...	15 37	11.38	25.50	12.35	34.20		Natural Cement
Limestone, ..	Union Bridge, Md	0.89	0.47	54.68	0.32	43.44		Lime
Limestone...	Woodville, O....	0.78	0.48	31.15	20.78	45.76		"
Oyster Shells.	Long Island Sound	3.30	0.25	52.14	0.25	41.61		"

TABLE III—ANALYSIS OF PORTLAND CEMENTS[1]

Where Made.	Made from	SiO_2.	Fe_2O_3.	Al_2O_3.	CaO.	MgO.	SO_3.	Loss.
1 New Jersey	Cement Rock and limestone	21.82	2.51	8.03	62.19	2.71	1.02	1.05
2 Penna.	Cement Rock and limestone	21.94	2.37	6.87	60.25	2.78	1.38	3.55
3 Michigan	Marl and clay	22.71	3.54	6.71	62.18	1.12	1.21	1.58
4 Ohio	Marl and clay	21.86	2.45	5.91	63.09	1.16	1.59	2.98
5 Virginia	Limestone and clay	21.31	2.81	6.54	63.01	2.71	1.42	2.01
6 Missouri	Limestone and clay	23.12	2.49	6.18	63.47	0.88	1.34	1.81
7 Penna.[2]	Limestone and clay	23.56	0.30	5.68	64.12	1.54	1.50	2.92
8 Illinois	Blast Furnace slag and limestone	22.41	2.51	8.12	62.01	1.68	1.40	1.02
9 Germany	.....	20.48	3.88	7.28	64.03	1.76	2.46	.....
10 Belgium	.....	23.87	2.27	6.91	64.49	1.04	0.88	.....
11 France	.....	22.30	3.50	8.50	62.80	0.45	0.70	.....
12 England	.....	19.75	5.01	7.48	61.39	1.28	0.96	.....
13 Germany[3]	Iron ore and limestone.	20.5	11.0	1.5	63.5	1.5	1.0	.....

[1] From Meade's "Portland Cement." [2] White Portland cement. [3] Sea-water cement.

TABLE IV—AVERAGE CHARACTERISTIC TESTS OF CEMENT IN THE UNITED STATES[1]

Class.	Materials used in Making Cement.	Specific Gravity.	Per Cent Passing through Sieve.		Time of Setting		Tensile Strength in Pounds per Square Inch.								
							Neat.					1 to 3.			
			No. 100.	No. 200.	Initial Min.	Hard Min.	1 Day.	7 Days.	28 Days.	6 Months.	12 Months.	7 Days.	28 Days.	6 Months.	12 Months.
Portland cement	Limestone and cement rock	3.14	93.7	75.2	155	392	371	675	750	789	945	239	315	366	442
	Limestone and clay or shale	3.13	95.0	76.2	172	341	341	696	825	916	919	252	353	401	403
	Limestone and granulated basic blast furnace slag	3.10	98.5	(a)	260	500	358	636	790	888	916	226	298	382	396
	Marl and clay or shale	3.11	94.0	79.2	151	357	328	670	772	780	790	269	352	385	395
	Average	3.12	95.3	76.9	185	398	350	669	784	843	893	247	330	384	409
Puzzolan or slag cement	Slaked lime and granulated basic blast furnace slag	2.88	99.4	95.0	145	452	120	432	502	651	(a)	189	260	272	(a)
												1 to 2			
Natural-rock cement	Argillaceous limestone	2.87	92.6	79.9	34	144	129	197	289	404	501	143	226	295	368

[1] From "Mineral Resources of the United States, Calendar Year 1904."

Lime. *Lime*, when good, is nearly pure calcium oxide, CaO, or a mixture of calcium and magnesium oxides. High calcium limes are stronger than those containing considerable percentages of magnesià. They are also better suited for mortar work, as they slake more readily. Magnesium limes, on the other hand, are better finishing limes, because they work smoother under the trowel. Pure lime, whether magnesium or not, is snow white. A very small percentage, however, of certain impurities

may give the lime a gray or yellow color. These impurities are chiefly iron and manganese. Through certain methods of burning the ash of the fuel may be introduced into the lime, causing discoloration. Wood-burned lime is usually much whiter than lime burned with coal.

Lime is made by burning limestone in suitable furnaces at a temperature sufficient to drive off all of its carbon dioxide, the reaction being $CaCO_3 = CaO + CO_2$. Theoretically, 806 calories per gram of lime are required to produce this change. This temperature is between 600° and 900° C. If a temperature much above 1200° C. is employed, the lime will be partially fused on the outside of the lumps. This causes the lime to be very slow in slaking, which is undesirable, as some of it may escape hydration in the mortar box and later will expand, or what is technically termed "blow" or "pop" in the wall. This latter manifests itself in small blisters in the finished work.

Intermittent Kilns. The types of kilns ordinarily employed in burning lime may be divided into two classes—intermittent kilns and continuous kilns. The intermittent kilns are primitive and uneconomical. They are, however, frequently used by farmers and other small producers of lime. Fig. 141 shows such a kiln. These kilns are usually made of large blocks of the limestone itself, though sometimes brick is used. The kilns are usually located on the side of a hill in order that the top may be accessible for charging by wagons and the bottom for drawing the lime and supplying the fuel. In charging the kilns an arch of large blocks of limestone is built 2 or 3 ft. from the ground, numerous small openings being left in it through which the flames may pass to the interior of the kiln. The fire is built under the arch, and on the top of the latter the limestone is piled, the charge usually consisting of stone from 2 to 8 ins. in diameter. After the kiln is full, a fire, usually of wood, is started, and the temperature gradually raised to prevent the limestone arch from crumbling. After about six or eight hours the temperature is raised to a red heat and maintained at this temperature for about two days. The kiln and contents are then allowed to cool and the lime drawn by pulling down the arch. There is a great waste of heat and time in these kilns, owing to the fact that the kiln must be cooled and reheated each time it is charged. Old kilns of this sort can usually be seen in any of the limestone farming regions.

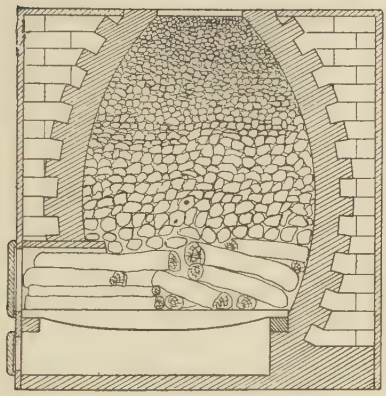

Fig. 141.

Continuous Kilns. Three different types of continuous kilns are employed: these are, (1) the vertical kiln with mixed feed, in which the

limestone and fuel are charged in alternate layers. (2) The vertical kiln with separate feed, in which the limestone and fuel are not brought in contact, and (3) the chamber or ring kiln.

Vertical Kilns. Vertical kilns with mixed feed are very similar to intermittent kilns, except that they are provided with an arrangement whereby the lime may be drawn at regular intervals from below. They are also usually somewhat larger than intermittent kilns. Like the latter, they are built on the side of a hill, usually of limestone blocks, and are sometimes lined with firebrick. In charging them, first a layer of anthracite coal or coke and then a layer of limestone is fed into the top. Fire is started at the bottom and works its way up. The process of charging and drawing the lime is continuous. These kilns are economical and, for the same size kiln, yield a larger quantity of product than do the vertical kilns with separate feed. On the other hand, the lime is contaminated by ash of the fuel, and the lime burned in these kilns must be carefully sorted in order to discard those lumps to which the fuel ash has adhered.

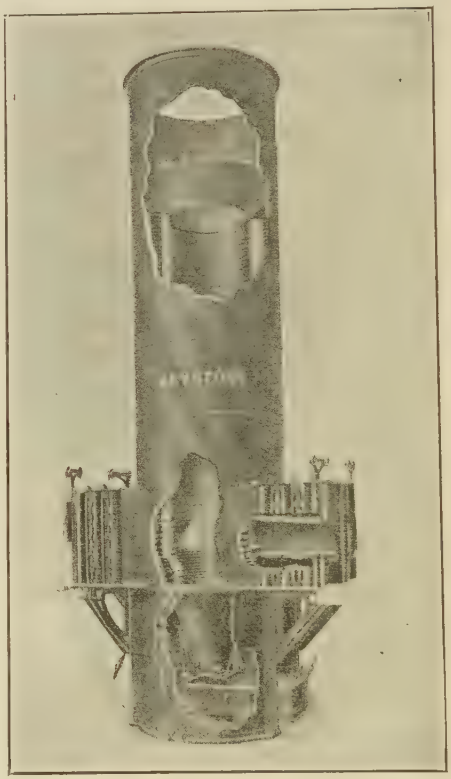

Fig. 142.

The vertical kiln with separate feed usually consists of a steel or reinforced concrete cylinder lined with firebrick. This is equipped with two fireplaces for the burning of the fuel, which are built into the sides of the kiln, so that the fuel is not mixed with the stone. The hot gases of combustion pass from the fire-box into the kiln, while the ash of the fuel drops through the grate bars into an ash-pit below, and does not mix with the lime. The kilns are usually constructed with hopper-shaped cooling chamber, set below the fire-box, which is closed by doors at the bottom. The cooling chamber holds about one draw of lime. Fig. 142 shows such a kiln. These kilns are from 6 to 10 ft. in cross-section, and from 40 to 50 ft. in height. They are usually charged by employing an incline and a cable hoist, by means of which the cars of limestone are drawn from the quarry to the top of the kilns. These kilns are sometimes provided with steel stacks in order to induce a better draft, as it has been found that the better the draft the greater facility with which the lime can be burned.

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Wood, oil and coal are employed for burning with these kilns. Wood is the best fuel for burning lime, as the wood burns with a longer flame of comparatively low temperature. This is an advantage, as it is essential that the heating should be conducted at a considerable distance inside the kiln without the temperature at the mouth of the fire-box being too high. The steam, which the wood introduces, also seems to be beneficial, and indeed some manufacturers prefer to use green wood because of the greater quantity of steam which it introduces. Wood-burned lime is whiter than that burned with coal.

Where coal is employed as a fuel, it is customary to wet this latter. A steam jet is also often employed, being inserted below the fire-box. The steam passing through the hot bed of coals is decomposed into hydrogen and carbon monoxide as follows: $H_2O+C=H_2+CO$. This gas is burned in the kiln itself, and hence carries the heating zone further into the latter.

Natural gas has also been used as a fuel, and producer gas is now being introduced to some extent. Considerable advantage is claimed for both, owing to the fact that the lime is not discolored by impurities, and also that these gases burn with a longer flame. The use of gas also saves the labor of stoking the grates.

Producer gas is now being applied to kilns of very large capacity. With hand-fired kilns of the type shown above the diameter cannot be increased beyond the limit to which the flames from the fire-box can reach effectively or the limestone in the center of the kiln will not be burned. The limiting diameter for such a kiln is about 6 to 7 ft. With gas, on the other hand, the kiln may be made much larger because the gas may be made to burn in all parts of the kiln. Usually this is done by having the producer gas enter through openings around the side of the kiln and the air through holes in the bottom of the kiln. The air is thus preheated by passing up through the hot lime, which it cools, coming in contact with the producer gas in the center of the kiln, where combustion takes place, spreading back to the gas openings. Gas-fired lime kilns are now built having capacities of from 40 to 60 tons per day.

Lime is also burned in rotary kilns similar to those described in the section on Portland cement. In using these kilns, the limestone is first crushed to pieces ranging in size from $\frac{1}{2}$ in. down to dust and fed into the kiln, which is heated by producer gas. These kilns are peculiarly adapted to burning highly crystalline stone, which would crumble when subjected to heat and so stop the draft of the vertical kiln, and to supplying lime for chemical purposes, where a fine lime is not objectionable. They are also used to burn lime from various lime-wastes, such as "lime-sludge" from paper mills and sugar purification. Lime is now burned from the calcium carbonate waste from caustic soda manufacture at a

number of plants by first passing the waste through some form of dewatering device such as a rotary continuous filter wheel, the waste being obtained from the latter in the form of a wet mud containing about 50 per cent water and then introducing it into the kiln. The recovered lime is very pure and usually contains some alkali otherwise lost, the percentage varying from 3 to 8 per cent of the lime recovered. This practice not only can be carried out generally for less than the cost of purchasing lump lime but it also disposes of a troublesome waste product.

Ring Kiln. The chamber or ring kiln is employed to some extent abroad, but has not been used in this country. It consists of a series of chambers which are built about a central stack and connected to the latter by flues. These chambers are alternately charged with fuel and limestone. Any chamber may be disconnected from the flue at will and also separated from those before and after it by partitions. As a chamber burns out, it is disconnected, the lime removed and the chamber recharged. As a chamber is charged it is connected with the stack and the flames passed through all the other chambers to this one, and thus to the stack. These kilns are economical of fuel, but require considerable labor.

Hydrated Lime. When lime is treated with water it combines with the water to form calcium hydroxide, $CaO+H_2O=Ca(OH)_2$. If the lime is free from impurities, it will take up 32.1 per cent of its own weight of water. A less amount of water than the theoretical quantity, however, is required to thoroughly hydrate lime, because of the impurities that are always found to a greater or less extent in all commercial limes. Until recently, lime was always hydrated or slaked by the mason just preparatory to its use. An excess of water was always used, and the calcium hydroxide formed with this a wet mass called lime putty. Recently, mechanical means of hydration have been introduced whereby the lime is hydrated by the manufacturer with just sufficient water to form the hydrate, leaving none in excess. This hydrated lime is a fine dry powder, practically all of which will pass through a 100-mesh screen. It is packed in paper bags or cloth sacks, and will keep indefinitely. It can be stored without danger of causing fire, which is not true of caustic line. Mortar made with it shows less danger of blowing or popping in the walls. It may be added to cement, when it makes the latter to some extent waterproof and more easy to trowel.

The process of manufacturing hydrated lime is briefly as follows: The lump lime is ground to small size. It is then mixed with just sufficient water, when it falls to a fine powder. The slaked lime is then sieved to separate out the unhydrated lumps or silicious cores from the latter.

The plan adopted in grinding the quicklime in the most successful hydrating plants consists in crushing the lime by means of a swing hammer mill or a Sturtevant open-door crusher. This reduces it to pieces about $\frac{1}{2}$ in. and under. Lime which is to be hydrated should not be burned

at such a high temperature as is ordinarily used. Fresh lime hydrates much more promptly than that which has been allowed to remain for some time in the air.

There are a number of processes and machines for mixing the lime with water which have been successfully used in hydrating. The two best known of these are the Kritzer and the Clyde hydrators.

The Clyde hydrator is a batch machine, in which a given quantity of lime—usually one ton—is placed. To this is added the proper quantity of water by means of a spray. The machine itself consists of a revolving pan provided with plows which stir up and mix the water and the lime. The water is weighed and added in a predetermined amount. When the operator judges the process to be complete, as is determined by the fluffiness of the powder, the lime is scraped from the pan through an opening in the center of the same into a hopper under the hydrator.

The Kritzer process is a continuous one. The hydrator consists of a number of cylinders one over the other, which are provided with paddles which revolve around a central shaft. The lime is fed into the upper cylinder in a continuous stream. Here water is spread upon it, the amount being regulated by means of a valve. The moist lime is worked by the paddles and passes through the upper cylinder to the next lower one, etc., and finally works its way out at one end of the bottom cylinder. It is now entirely hydrated and dry. The steam from the lower cylinders passes to the upper ones, and helps to hydrate the lime. The amount of water to be added in each case is determined by experience. The more calcium oxide the lime contains, the more water must be added.

After slaking, the lime is in the form of a very fluffy powder, all of which will pass through a very fine sieve. Mixed with this hydrated lime, however, are larger pieces or "cores" which consist of unburned limestone, silicious matter which has been partially vitrified, and overburned lime which has not been hydrated. The last two of these if left in the lime will cause trouble, because when the lime is applied to plastering they will not slake when water is mixed with the hydrate but will do so in time. Now when the lime slakes it expands and hence wherever there was one of these cores in the wall a little blister will occur. It is therefore usual to either separate out these cores or else to grind them so finely that when water is added to the hydrate they will slake before the plaster sets. Where they are separated out, this is usually done by means of an air separator of the Raymond type, although Newaygo and shaking screens are used in some of the older and smaller mills. If the cores are pulverized this is usually done by passing the lime directly from the hydrator through some type of pulverizer such as a Raymond "beater mill," a tube mill, a Bonnot mill or a Fuller mill. In either event it is now ready for the market.

Hydrated lime is now packed in paper and cloth bags. Automatic bagging machines have been devised which allow it to be packed very

rapidly in bags, which are pasted shut or tied before the lime is placed in them, this latter being done by means of a valve in one corner of the bags. These paper bags present a square appearance, and not the ragged end of the hand-tied bag.

Hydraulic Lime. Limestones containing appreciable amounts of impurities sufficient to give the calcined product hydraulic properties, but insufficient to take up all the lime present, make, when burned, hydraulic limes. They form an intermediate product between ordinary lime and natural cement. These products range from feebly hydraulic limes to limes which harden quite satisfactorily under water. At one time these limes were manufactured to a large extent in Europe. They have never, however, been manufactured in any quantity in this country. They are made by burning limestone containing from 10 to 17 per cent silica, alumina and iron and from 40 to 45 per cent lime. Magnesia may replace lime to a considerable extent. Hydraulic lime slakes with water just as does ordinary lime, only much more slowly.

Grappier Cements. These are obtained by grinding the hard cores which are obtained in the manufacture of hydraulic lime, and consist of that portion of the hydraulic lime which does not slake when water is added. *La Farge* cement is of this class, and is imported extensively in this country, owing to its light color and the fact that it does not stain marble and other building stones as does Portland cement and natural cement.

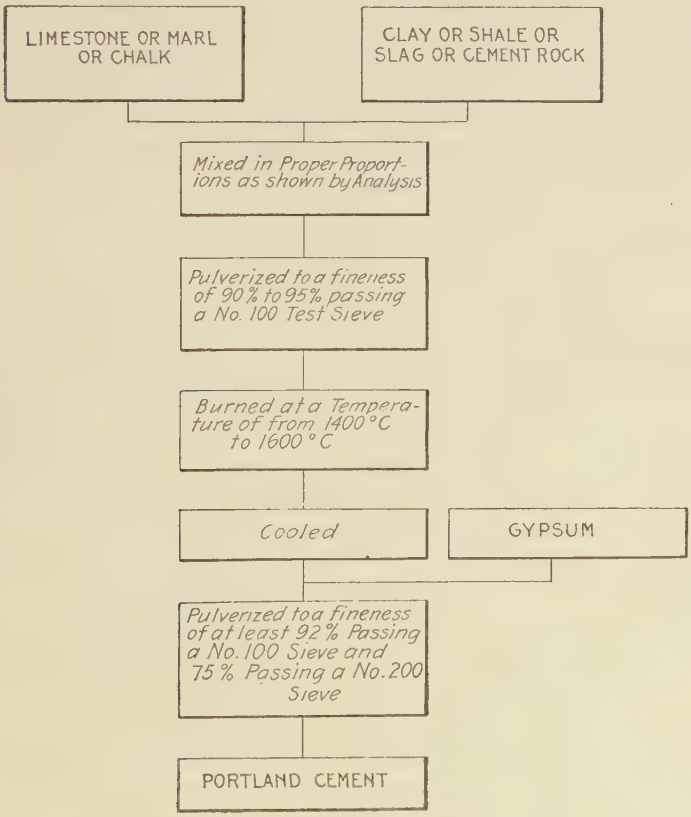
Natural Cement. Natural cement was at one time manufactured extensively in this country. Owing to the cheapness, however, with which Portland cement can be manufactured, it is being replaced by this latter. Natural cements are produced by burning and subsequently grinding clayey or argillaceous limestones, which are natural mixtures of calcium carbonate and clay. These limestones usually carry from 13 to 35 per cent clayey matter ($SiO_2+Al_2O_3+Fe_2O_3$), and often a considerable percentage of magnesia, which seems to be interchangeable with lime and to replace the latter without disadvantage.

The kilns used for burning natural cement are very similar to those used for burning lime. The best kiln consists of a steel cylinder lined with firebrick and provided with an opening at the bottom through which the burned material may be drawn from the kiln. The kiln is continuous in operation and the charging is done by introducing at the top alternate layers of limestone and fuel. This latter usually consists of small size anthracite coal or coke. The temperature of burning is usually between 1000° and 1200° C.

After passing through the kilns the burned material presents the appearance of a soft yellowish-brown mass. It is then ground to a fine powder. As it is quite soft, this is usually done with burr-stones or in tube mills. Recently, however, excellent results have been obtained by grinding the natural cements to an extreme degree of fineness by the employment of some of the more modern mills, such as the Fuller-Lehigh

mill. The grinding of the clinker should be at least so fine that 90 per cent will pass through a 100-mesh screen.

Portland Cement is now considered next to iron and steel as our most important building material, and the production of this in the United States now amounts to over ninety millions of barrels annually. Portland cement is manufactured by combining a material high in lime such as limestone or marl with one in which silica, iron oxide and alumina are the chief constitutents, such as clay or shale. The raw materials are intimately mixed by finely grinding the two. The fine powder is then subjected to a temperature of from 1400°–1600° C., when a sintering or semi-fusion takes place and the mixture rolls up into little balls varying in size from that of a walnut down to that of wheat, with an occasional larger piece and some fine sand. After cooling, these lumps or " clinkers " are mixed with a small amount (2–3 per cent) of gypsum and finely pulverized. The resulting powder is Portland cement. The following diagram explains this graphically:


LIMESTONE OR MARL OR CHALK
CLAY OR SHALE OR SLAG OR CEMENT ROCK
Mixed in Proper Proportions as shown by Analysis
Pulverized to a fineness of 90% to 95% passing a No. 100 Test Sieve
Burned at a Temperature of from 1400°C to 1600°C
Cooled
GYPSUM
Pulverized to a fineness of at least 92% Passing a No. 100 Sieve and 75% Passing a No. 200 Sieve
PORTLAND CEMENT

It is now generally agreed that Portland cement is a solid solution of lime in a magma of ortho-silicates and ortho-aluminates of lime.

It is therefore impossible to ascribe to Portland cement any definite chemical formula. The composition of Portland cement, however, has a great bearing upon its physical properties. The conditions of manufacture, particularly as to burning and grinding, also influence this. The composition of Portland cement of good quality is usually within the following limits:

COMPOSITION OF PORTLAND CEMENT

	Limits.	Average.
Silica	20–24 %	22.0 %
Iron oxide	2–4 "	2.5 "
Alumina	5–9 "	7.5 "
Lime	60–64.5 "	62.0 "
Magnesia	1–4 "	2.5 "
Sulphur trioxide	1–1.75 "	1.5 "

Practical experience has shown that the essential elements in cement are lime, silica and alumina. Iron oxide is present in nearly all clays and shales, and hence is always present in cement. It has a definite advantage, in that it assists in burning and lowers the temperature of the latter process. Cement containing no iron is white, but rather hard to burn. The proportions of a good cement should satisfy the following ratios:

$$\frac{\text{Per cent lime}}{\text{Per cent silica}+\text{per cent iron oxide}+\text{per cent alumina}} = 1.9 \text{ to } 2.1.$$

$$\frac{\text{Per cent silica}}{\text{Per cent alumina}} = 2.5 \text{ to } 4.$$

In the manufacture of Portland cement great care is taken to see that the composition satisfies the above. If too much lime is present the cement will be "unsound"—that is, in time concrete made from it will expand and crack. If too little lime is present the concrete will be low in strength and may "set" quickly—that is, harden before the masons have a chance to place it in the forms. Cement in which alumina is high is also apt to be quick setting, and is hard to burn uniformly. High silica cements are usually very slow hardening, and do not attain their full strength for a considerable period. Cements should not contain more than 5 per cent magnesia, or 2 per cent SO_3. The latter is usually introduced in the form of gypsum, and is added to regulate the setting time of the cement.

The materials from which Portland cement is manufactured may be divided into two classes: those which supply the lime and those which supply the silica, iron oxide and alumina. The first are termed calcareous and the second argillaceous. The following groups show the principal materials used in the manufacture of Portland cement.

Calcareous Materials.		Argillaceous Materials.
Limestone	Cement Rock	Clay
Marl		Shale
Chalk		Slate
Alkali waste		Blast furnace slag

The cement rock is an argillaceous limestone which contains usually between 65 and 80 per cent carbonate of lime. If it contains more than 75 per cent it is necessary to add clay, shale or slate to it in order to make a satisfactory mixture for burning. If it contains less than 75 per cent it will be necessary to add limestone for a similar purpose.

Limestone is usually mixed with clay or shale, marls and chalks with clay or shale. Blast furnace slag is used with limestone. Alkali waste (or precipitated $CaCO_3$, obtained from the manufacture of caustic soda) was at one time mixed with clay, but is not now employed for the manufacture of Portland cement.

Limestones, marls and chalks which are to be used in the manufacture of Portland cement should contain less than $2\frac{1}{2}$ per cent magnesia and preferably not more than 3 or 4 per cent silica, iron oxide and alumina combined. Clay, shales and slates should all have at least $2\frac{1}{2}$ and not more than 4 times as much silica as alumina. Exceptions to this are in the case of a high silica limestone, with which a high alumina clay may be used to advantage, since all that is necessary is that the mixture shall satisfy the requirements expressed by the above formulas for the composition of Portland cement.

Crushing and Pulverizing. Three processes are employed for the manufacture of Portland cement—the dry process, a semi-wet process, and a wet process. The dry process is employed exclusively for the manufacture of cement from cement rock and limestone, and also from limestone and shale and limestone and blast furnace slag. The semi-wet process is employed at a few plants manufacturing cement from limestone and clay. The wet process is employed by plants using marl and clay.

The dry process is an American invention, and is much the most economical of the three. In this process the materials are dried and mixed, ground to such a degree of fineness that at least 92 per cent of the powdered mixture will pass a 100-mesh sieve, and burned at a temperature of approximately 1400 to 1600° C. The resulting clinker is then mixed with 2 to 3 per cent gypsum, and ground so fine that at least 92 per cent will pass the 100-mesh sieve. The resulting product is Portland cement.

In the semi-wet process materials are ground, dried and mixed with a small proportion of water and introduced into the kiln in the form of a wet paste. The resulting clinker is ground with gypsum just as in the dry process. In the wet process the wet marl and clay are ground together without drying, and often, after having more water actually added to

them, weighed and introduced into the kilns in the form of a thin mud, called slurry, containing 50 to 60 per cent water, and the clinker ground as before.

Limestone, cement rock and shale are quarried, while clay is taken from beds and marl is dredged from under water. The stone is usually blasted down in benches, an attempt being made to shatter the rock as much as possible. It is then loaded either by steam shovels or by hand into cars and conveyed to the mill. In the dry process the product goes from the quarry to the storehouse, and here it is treated in one of a number of ways. The older method was to dump the product in large piles which were analyzed, and from these analyses the necessary mixture of limestone and clay was calculated. The rock was then loaded on buggies or barrows and wheeled to the crusher after being weighed, where it met another buggy or barrow loaded with the other material to be added. The two barrows were then dumped into the crusher together, one after the other. Another method employed is to weigh the rock as it comes from the quarry and add to the car containing it the proper amount of limestone or clay. This is then dumped into the crusher. In the third system rocks are crushed and even partially ground separately and conveyed into bins, where they remain until the contents of the latter are analyzed. They are then drawn out and mixed in the proper proportions.

The crushing is nearly always done in a gyratory or Gates crusher. The jaw or Blake crusher was at one time used to some extent; but now the Gates crusher, owing to the fact that it has much greater capacity and does not clog as easily, is almost universally used. After being crushed the rock is usually dried. This is done by means of rotary driers. These are cylinders of sheet steel from 4 to 6 ft. in diameter and from 40 to 60 ft. in length. They are unlined, and are usually provided with channel irons bolted to the inside to act as shelves, to carry the rock up and drop it through the hot gases. The driers are heated by a coal fire at the lower end or else by the waste gases from the rotary kilns. They are similar in construction to the rotary kilns described farther on, except that they are smaller and are not lined with firebrick.

Marl is usually conveyed to the mill by cars, barges or pipe lines in the form of a thin mud. It is passed through some form of pug mill provided with screens which separate out of it any sticks, stones, etc. From the pug mill it passes to large concrete basins or steel tanks, where it is sampled. The clay is usually dried to facilitate chemical work of making a proper mixture, and disintegrated in dry pans. The marl is either measured or weighed, and the proper amount of clay added. From the measuring tank the mixture is pumped into a pug mill and thoroughly mixed. From the pug mill the materials run into large vats, where the mixture is sampled and analyzed, and if not of correct composition more clay is added. The contents of all vats are kept in continual agitation by means of compressed air or mechanical stirrers. When the material

has become of correct chemical composition it is passed on for the final grinding, which is done in tube mills.

The grinding of dry materials is usually done in two stages. A number of mills are upon the market for doing this grinding. For the preliminary grinding the ball mill, rolls and the hammer-mill are used, while for final pulverizing the Fuller-Lehigh mill, the tube mill, the Griffin mill, and the Huntington mill are the ones usually employed. The ball mill consists of a drum filled with steel balls. The drum is lined first with steel plates which lap one over the other to form steps. As the drum revolves the balls fall over the steps, and so pound the material to pieces. The partially crushed material drops through holes in the plates on to perforated steel screens built around the entire circumference of the drum. These screens take out the very coarse particles and return them to the inside of the drum. The finer ones drop on another set of screens made of woven wire cloth, and these separate the fully ground material from the coarse and return the latter back to the mill. The fully ground material falls into a dust-proof casing which entirely surrounds the mill, and then down to the conveyor under the latter, which carries the coarsely ground material on to the next step. The ends of the drum are formed by circular plates, and the material is fed in through a large opening in the center of one of these. The material is fed in by means of automatic feeders, which regulate the quantity of the material admitted to the mill. The size of the product is regulated entirely by the fineness of the last set of screens. When preparing for the tube mill, these are usually 16 to 20 mesh, while if preparing for the Fuller and Griffin mills, all screens are removed. The product of a ball mill equipped with 16-mesh screens will usually, about half of it, pass a 100-mesh screen.

The kominuter is a modification of the ball mill. It consists of a drum about the same diameter as a ball mill, but somewhat longer than the latter. The kominuter is lined just as is the ball mill, with steel plates which are arranged to lap and form steps. The drum is surrounded by a coarse screen tilting toward the feed end. The material enters through an opening at one end, and is pounded to pieces by the balls. It does not fall out through holes in the plates at once, however, but travels through the full length of the drum, and passes through openings at the opposite end, on to screens. The underground material is returned to the mill by means of S-shaped pipes at one end.

The Williams mill consists of hinged hammers which revolve around a horizontal shaft. These crush the material and pass it out through a grid, the bars of the grid serving as part of the crushing surface.

The tube mill consists of a cylinder 20 to 22 ft. long and from 5 ft. to 8 ft. in diameter, filled with flint pebbles or steel or chilled iron slugs. The cylinder is lined with some hard substance, such as armor plate, chilled iron, quartz, or trap-rock, and revolves at a speed of from 25 to 27 revolutions per minute. The material is fed in through a hollow shaft, and leaves

either in the same manner at the opposite end or else through a grating at the perimeter of the end. The flint pebbles are imported from Europe, and the wear on them is not great. Slugs give a greater output than pebbles but require much more power. Material is usually fed in at a regular rate by means of a screw conveyor operated by means of some form of speed-regulating device. The fineness of the product is controlled entirely by the amount of material fed into it.

The Fuller-Lehigh Pulverizer mill, Fig. 11, consists of a horizontal ring or die against which revolve four balls. The balls are propelled by means of pushers. The die and pushers are chilled charcoal iron castings. The balls are of steel forgings. They revolve rapidly and hence press against the die with enormous centrifugal force. The material to be ground is fed into the hopper which serves the feeder. The material discharged by the feeder falls down into the pan of the mill situated below the die, and is drawn up from this in between the rapidly revolving balls and stationary die by means of currents induced by fans placed in the chamber above the die. The material is pulverized by the rolling of the balls against the die, the grinding action being similar to that of a mortar and pestle. The finely pulverized material is sucked upwards by means of the fans and out through the screens. The material passing through the screen falls down between this screen and the outer casing, and is discharged from the mill through the discharge spout, which may be placed at any one of the four quarters of the mill. The feed to the mill, and consequently the fineness of the products, may be controlled in two ways: either by a slide on the hopper or by means of the stepped pulley, connected to the screw conveyor by gearing. The mill is provided with two screens, one—the inner—of 1-in. mesh and made of very heavy wire to protect the outer one. The outer screen does not really screen, but merely controls the draft of air, and hence the fineness, since the greater the velocity the greater the carrying power of the air, and hence the coarser the product.

The Griffin mill is somewhat similar to the Fuller-Lehigh mill in operation. It consists of a steel die against which a roll also of steel is made to revolve, and it is between these two that the material is ground. The roll is suspended by a shaft from a spider, and actuated by a pulley and a universal joint. The fully ground material is sucked up and forced through the screens. The coarse particles fall back into the pans of the mill and are thrown up between the roll and the die by means of a plow attached to the roll. The finished product passes through the screen and travels from these to the outer casing and thence through openings in the base of the mill to screw conveyors.

The degree of fineness to which the raw material is to be ground depends entirely upon conditions. It is stated as a general rule it should never be ground coarser than 90 per cent through the 100-mesh sieve, and in most cases 95 to 98 per cent is required to produce a sound cement.

The finer the grinding the more perfect the combination between the silica, the alumina, the iron and the lime. If the raw materials are not finely enough ground, the cement will be unsound—that is, some of the lime will not combine and will cause the cement to disintegrate.

The material is usually carried from one part of the process to another by mechanical means. Belt conveyors are used for the coarser material and screw conveyors for the finely pulverized. Marl and slurry are pumped through pipe lines, sufficient water being added to make them flow easily.

In the early days of the American Portland cement industry, the burning was done in intermittent upright kilns, similar to those used for burning lime. These were soon improved, so as to economize fuel by making them continuous in action. This allowed the charge to receive the waste heat from the clinkering of the cement, and the air for combustion to be preheated, by passing through the fully-burned material, this serving also to cool the latter. These upright kilns required that the material be moulded into small balls or bricks, which of course necessitated much hand labor. When the material to be burned was not plastic, like a mixture of limestone and clay, it was further necessary to add a binder, such as coal tar or cement itself. About 1887, a rotary kiln was introduced, and this is the form of kiln now universally used in this country, as it allows the material to be fed directly into it, either in the form of a powder or a slurry, thus saving much labor.

Rotary Kiln. The rotary kiln, in its usual form, Fig. 143, consists of a cylinder, from 6 to 8 feet in diameter and from 60 to 150 ft. long, made of sheet steel and lined with firebrick. The steel sheets are from $\frac{1}{2}$ to $\frac{9}{16}$ in. thick, and are held together by single-strap butt joints. This long cylinder is supported at a very slight pitch ($\frac{3}{4}$ in. to the foot) from the horizontal, on two or more tires made of rolled steel, which in turn revolve on heavy friction rollers. The kiln is driven at a speed of from one turn a minute to a turn in two minutes by a girth-gear situated near its middle, and a train of gears. The power is supplied by either a line shaft or a motor. The upper end of the kiln projects into a brick flue, which is surmounted by a steel stack, also lined with firebrick for its entire height. The flue is provided with a door at the bottom, which serves not only to allow the flue to be cleared of the dust which accumulates in it, but also as a damper to control the draft of the kiln.

The material to be burned is usually fed into the kiln through a horizontal water-jacketed screw conveyor, or else spouted into it through an inclined cast-iron pipe. When slurry is to be burned this is pumped into the kiln. The dry raw material is kept in large steel bins above the feeding device, while slurry is stored in vats, in order, in either case, to have on hand a constant and regular supply. The raw material feeding device is usually attached to the driving gear of the kiln, so that when the kiln stops the feed also stops.

The lower end of the kiln is closed by a firebrick hood. This is usually

mounted on rollers, so it can be moved away from the kiln when the latter has to be relined. The hood is provided with two openings: one for the entrance and support of the fuel-burning apparatus, and the other for observing the operation, temperature, etc., of the kiln, and through which bars may be inserted to break up the rings of material which form, and to patch and repair the lining. The lower part of the hood is left partly open. Through this opening the clinker falls out and most of the air for combustion enters.

The kiln is heated by a jet of burning fuel, usually powdered coal, but sometimes (as in Kansas) natural gas and (as in California) fuel oil are used. The coal is blown in by a blast of air supplied by either a fan or air compressor. If the fan is used, about 20 per cent of the air

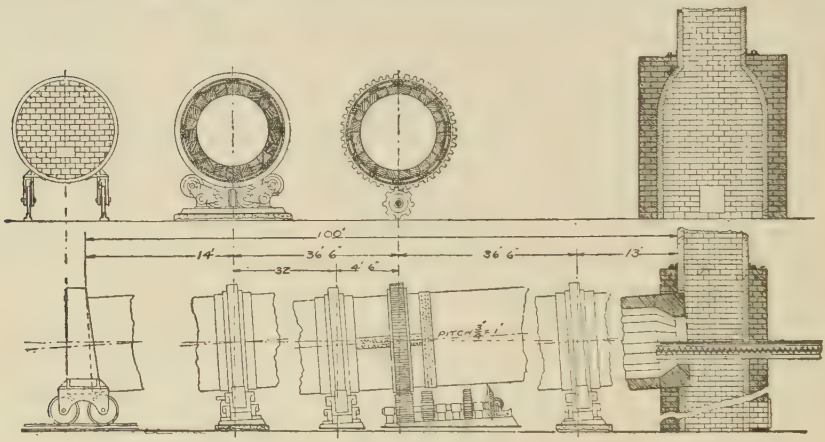


Fig. 143.

necessary for combustion is supplied this way. If the compressor is employed, only 5 to 10 per cent of the air is delivered by the compressor.

The necessary temperature of the hottest part of the kiln is about 1400° C., and is rarely ever less than 1600° C. To properly maintain this temperature, about 80 lbs. to 160 lbs. of fuel are required per barrel of cement, the actual amount depending on the coal itself, the material to be burned and the dimensions of the kiln. The longer the kiln, the greater economy it will show. Dry materials require much less coal than slurry. With limestone and shale mixture, and a kiln 100 ft. long by 7 ft. in diameter, the coal consumption will amount to about 90 lbs. of good gas slack per barrel. A kiln 60 ft. long by 6 ft. in diameter will, on the other hand, require about 110 lbs. of this material per barrel.

Of the heat supplied to the kiln by the burning of the coal, by far the larger proportion is wasted. About 50 to 75 per cent of it is carried off by the waste gases of the stack, and from 10 to 15 per cent by the hot clinker falling from the lower end of the kiln. The gases enter the stack at from 600° to 800° C., and the clinker leaves the kiln at not much

under 1200° C. If the kiln could be made to show the same economy as is common in good boiler practice, a barrel of cement could be burned with 25 lbs. of coal.

As we have said the gases leave the dry process kiln at about 800° C. A number of plants have recently installed boilers at the end of the kilns and lead the waste gases through these. By so doing they obtain about one-third to one-half the power needed in the plant from the kilns. Water-tube boilers are employed and also an elaborate system of flues in which some of the dust in the waste gases is deposited. The flow of gases through the boilers at a high velocity is one of the requisites for successful employment of the waste gases for steam generation and this is obtained by means of an inducted draft fan.

The raw material as it enters the kiln contains about 33 per cent carbon dioxide. For the first 30 ft. of its journey through a 100-ft. kiln, it is merely heated up, and whatever water it contains is driven off. In the next 40 ft. it loses all its carbon dioxide and sticks together, forming small, soft, lemon-yellow balls, which, as they reach the hottest part of the kiln—the last 30 ft.—partially vitrify, become rough and hard, and turn to a greenish-black color. Properly burned Portland cement clinker is greenish-black in color, of vitreous luster, and, usually, when just cooled, sparkles with little bright glistening specks. It forms in lumps from the size of a walnut to hardly more than dust, with here and there a larger lump. Under-burned clinker is more or less soft, is irregular in shape, and not so black as the well-burned material. Under-burned clinker usually shows soft-brown centers, but hard-brown centers are due to very hard burning.

When coal is used for burning, this is pulverized in mills similar to those used for grinding the raw materials. It is, however, first crushed by passing it through rolls or pot crushers, and then dried in rotary driers of special type. The mills most used for coal pulverizing are the Fuller mill and the tube mill. The latter need not be preceded by a ball mill. The coal should be pulverized so that 90 per cent of it will pass a sieve having 100 meshes to the linear inch, and should contain from 30 to 45 per cent volatile matter.

Normally in the dry process from 3 to 5 per cent and in the wet process from 2 to 3 per cent of the raw material is carried away in the exit gases of the kiln as dust. Various schemes have been tried with a view to eliminating the dust such as settling chambers, water sprays and electrical precipitation. The latter is the only method, however, which is used to any extent. Several installations of this system are now in operation. The dust collected by the latter is found to contain considerable potash some of which is water-soluble and can be used for fertilizer. About half the potash in the raw material is volatilized in the kiln and this can be collected by means of electrical precipitation. Ordinarily about 2 lbs. of K_2O are obtained per barrel of cement produced, the dust generally

containing from 10 to 15 per cent total K_2O and from 2 to 10 per cent water-soluble K_2O.

Cooler. As the clinker leaves the kiln at about 2000° F., it is entirely too hot to grind, and must be cooled to ordinary air temperatures. This can be done by allowing it to lie in piles; but, as it is a slow way of doing it, mechanical devices are usually resorted to. These may consist of either revolving horizontal cylinders or vertical stationary coolers. The former consist of steel cylinders provided with angle irons on their insides to carry the material up and drop it through the current of air passing through the cylinders. They are mounted on tires and rollers, just as are kilns and driers, and revolve at a speed of about a turn or two a minute. They are usually placed below the kiln, and the clinker falls from the kiln into them. The air for cooling is also drawn through them into the kiln by the draft of the latter. They thus serve not only to cool the clinker, but also to preheat the air entering the kiln.

The upright cooler, shown in Fig. 144, is almost universally used in the Lehigh district. It consists of an upright steel cylinder, 8 ft. in diameter and 35 feet high, provided with baffle plates and shelves. As the clinker falls over these, it meets a current of air blown in through a perforated pipe running up through the center of the cylinder, and is thus cooled. The clinker is carried from the kiln into these latter coolers by means of bucket elevators, water being run into the buckets to keep them cool. This also suddenly chills the clinker and makes it brittle and easier to grind.

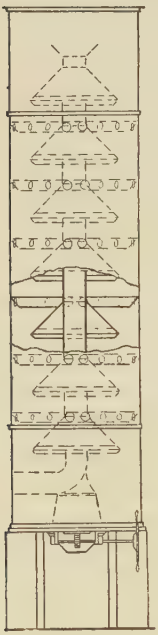


Fig. 144.

After cooling, the clinker is ground in Griffin mills or ball and tube mills. In the case of the Griffin mills, it is usually found more economical to crush the clinker down to pea size by a set of rolls, before feeding to the mills. Kent mills and air separators, and also Kent mills which grind as preparation for the other mills, are used to a limited extent. The clinker should be ground so fine that at least 92 per cent of it passes a sieve having 100 meshes to the linear inch.

In order to regulate the set of the cement, since clinker ground alone would set very rapidly, it is necessary to add to it calcium sulphate in some form or other, usually as gypsum, or plaster of Paris. As this can be most easily mixed with the cement during grinding, it is the usual practice to add the retarder to the clinker before the latter is ground, and to grind the two together. The amounts of gypsum or plaster of Paris used is usually about 2 or 3 per cent of the weight of the clinker.

After passing through the clinker mills, the cement is conveyed to the stock house. This usually consists of a long, low building of wood,

stone or concrete, cut up into bins. The cement is brought in by an overhead screw-conveyor and dropped into any desired bin by means of a slide in the bottom of the conveyor trough. A screw-conveyor also runs under the floor of the stock house, at the ends of the bins. The latter are provided with removable board ends, and, when it is desired to pack from any bin, these ends are removed and the cement allowed to run into the screw-conveyor. When the cement ceases to run, it is necessary to either pull it into the conveyor with a broad-blade hoe, or else to wheel it there in barrows. The screw-conveyors then carry it to the packing machines, which are similar to those used in flour mills. At some of the newer plants reinforced concrete silos are used for storing the cement.

Cement is packed into barrels holding 380 lbs., or into paper or cloth bags holding 95 lbs. each. The cement is packed as shipped, and the bags or barrels are trucked directly to the cars. For this reason the packing-room floor is on a level with the floor of the cars to be loaded, and these latter are brought alongside of the room. A shed roof should run out over the cars, so the loading can be done in stormy weather. Cars usually hold from 100 bbls. to 250 bbls. of cement, with 150 bbls. for an average.

Much more cement is packed in cloth bags than in anything else. In the case of these bags, the consumer is charged with the value of the bag, and credited by a certain amount if the bag is returned in good condition. The bags are all marked with the brand label of the manufacturer, and so each manufacturer knows his own bags. Barrels and paper bags are sold to the customer, and are not returnable.

Plaster of Paris. Plaster of Paris is made from gypsum by heating the latter to a temperature of between 212 and 400° F., when three-quarters of the water of crystallization of the gypsum is driven off, the resulting product being plaster of Paris.

$$2(CaSO_4 2H_2O) = (CaSO_4)_2H_2O + 3H_2O.$$

In actual practice the temperatures employed to bring about this reaction are 330 to 395° F. If gypsum is heated above 400° F., it loses all of its water of combination and becomes anhydrous sulphate of lime, the latter being the basis of hard finish plaster, floor plaster, Keene's cement, etc.

When plaster of Paris is mixed with water it sets or hardens very promptly, this change being due to absorption of water, forming gypsum again.

$$(CaSO_4)_2H_2O + 3H_2O = 2CaSO_4 2H_2O.$$

A pure plaster of Paris will normally harden or set in from five to fifteen minutes after having been mixed with water. If the gypsum from which the plaster is made contains impurities, the set will be much slower than

this. Plaster to be used for building purposes must be slow setting. For ornamental use, it must also be white; and since the impurities usually render the plaster slightly colored, it is the common practice to add retarders to the plaster before placing the same upon the market. The materials used as retarders are usually of a colloidal nature, such as glue, sawdust, blood, packing-house tankage, etc. Retarders now used are usually made by digesting hair with caustic soda. If a very quick-setting plaster is desired, crystallized salts are employed, such as common salt, sodium sulphate, sodium carbonate, etc.

Gypsum, the raw material from which plaster is made, is, when pure, a hydrous sulphate of lime, $CaSO_4 2H_2O$. As mined, however, gypsum usually contains a considerable percentage of impurities, the chief of which are clay, calcium carbonate and magnesium carbonate. The following table gives the analyses of some American gypsums:

Locality.	SiO_2	Fe_2O_3	$CaCO_3$	MCO_3	$CaSO_4$	H_2O
Nova Scotia	0.10	0.02	1.04	trace	78.60	20.13
Kansas	0.35	0.12	0.10	0.25	78.73	20.52
Michigan	1.24	0.50	2.38	....	77.19	19.03
Kansas	2.17	0.24	2.66	0.95	75.11	19.40
Oklahoma	17.95	1.43	....	....	61.00	18.44
Indian Terr.	10.67	0.60	10.21	1.10	59.46	16.59

Impure earthy gypsum, such as that shown in the last two analyses of the above table, is known in the trade as gypsum earth or gypsite.

Gypsum occurs usually in the form of beds, frequently associated with deposits of rock salt, and almost always interstratified with beds of limestone and shale. The beds, of course, vary greatly in extent and thickness, some of them being as thick as 60 ft., while a great many of them are very much smaller than this. The principal gypsum deposits found in this country lie in three geological series—namely, the Salina group of the Silurian, the Lower Carboniferous and the Permian. The localities in this country which produce gypsum are central and western New York, southwest Virginia, northern Ohio, Michigan, and a great many of the western states, Kansas and Oklahoma being large producers.

The usual plan of working the gypsum deposits is by mining, and deposits seldom lie near enough to the surface for quarrying. For the most part the mining methods are crude.

The operation of manufacturing plaster of Paris from gypsum consists in first crushing and grinding the gypsum, then calcining the ground product, and finally pulverizing the calcined product, after which the retarders are added. In some plants, the gypsum is merely crushed and calcined, the calcined rock then being ground very finely. Where the kettle process is employed, the pulverizing, however, is done before the calcining. Where the rotary cylinder process of calcining is used, the pulverizing is done after the calcining.

The process of preparing the gypsum for the kettles usually consists in first crushing it to such a size that it will pass a 2-in. screen. The crushers employed for this purpose are of both the Blake and the Gates types. The former type is especially devised for cracking gypsum. After the coarse crushers, the gypsum is further reduced by means of a double cone or pot crusher. These crack the gypsum to such a size that most of it will pass a $\frac{1}{2}$-in. ring screen. From the pot crusher the gypsum passes to buhrstones, rock-emery mills or in the newer plants Raymond mills. These reduce the gypsum so that about 60 to 95 per cent of it will pass a No. 100 mesh sieve, the finer the better the product. It is then ready to be fed to the kettles.

Gypsum Kettle. The gypsum kettle consists of a steel cylinder set in brick work. The bottom of the kettle is made of cast iron, and is convex in shape. The bottom has a thickness of about $\frac{3}{4}$ in. at the edges and 4 in. at the crown. This kettle bottom is a very important part of the apparatus, and is the part which seems to need oftenest repairing. If made from ordinary scrap iron they are apt to crack. Sheet steel has been tried, but does not seem to be as good as the cast iron. The kettle itself, which is placed on the kettle bottom, is made of boiler iron, $\frac{3}{8}$ to $\frac{5}{8}$ in. thick. It is from 8 to 10 ft. in diameter and 6 to 8 ft. deep. A kettle of this size will hold from 7 to 12 tons of pulverized gypsum and produce from $5\frac{1}{2}$ to 10 tons of plaster. The kettle is provided with from two to four flues, 12 in. in diameter, placed horizontally about 8 in. above the crown of the kettle bottom, and separated externally about 6 in. The kettle is surrounded by brick work, so that the heated gas from the fire may rise around its sides and through the flues. The top of the kettle is covered with sheet iron, has a movable door and a vent to carry off the water. The two kettles are usually placed side by side and work in pairs.

It is necessary that the material in the kettle be continually agitated. For this purpose the kettle is provided with a stirrer, which is actuated by a vertical pinion wheel and a line shaft. The stirrer itself consists of a cross arm which is curved to conform to the bottom of the kettle and provided with either paddles or a chain which drags along the kettle bottom. The stirrer is run at about 15 to 20 revolutions per minute, and is so arranged as to throw the material towards the center of the kettle. About 15 or 20 horse-power is required to operate the stirrer. If the gypsum is not stirred the charge will settle down and become hard. The bottom would be also immediately melted out of the kettle. In starting a kettle the heat is gradually applied, the crude material is fed in through the charging door and the stirrer put in motion. The material is added gradually until the kettle is full. As the temperature rises, the water begins to be driven off. The mechanically held water is first driven off at a temperature of 212° F., after which the contents of the kettle remain fairly quiet until a temperature of 290° F. is reached, when the material

begins to boil and the water of combination begins to be driven off. An expert calciner can tell by the way in which the charge boils when the process is finished. When the material has been calcined sufficiently it is run by means of a small grate in the side of the kettle into a pit.

In burning pure gypsum the temperature rarely exceeds 340° F. Thermometers may here be used to advantage. In gypsite plants, however, a higher temperature is required, which may sometimes reach as high as 390° F. Here, owing to the complexity of the material, the proper temperature for calcining varies, and thermometers cannot be used.

The gypsum kettles are arranged in pairs, with a pit to each pair of kettles, in order that the pit may be emptied from one charge while the other is being cooked. The calcined material is carried from the pit, by means of an elevator, to a bolting reel, where the coarse material, usually amounting to only a few per cent, is screened out, sent back to buhrstones and reground. From the bolting reel the material is conveyed to a storage bin. There are usually several of these in order to separate the runs of different days.

Cummer System. The Cummer system of calcining consists in first partially crushing the material, so that it will pass a 1-in. ring screen. The gypsum crushed to this state is fed mechanically into a rotary drier or calciner. The material, in passing through the calciner, is heated to a temperature of from 350° to 400° F., the exact temperature depending upon the nature of the rock. From the drier the gypsum is carried into a storage bin. These bins are built of vitrified brick or concrete, so that they will not take fire or absorb the moisture given off by the gypsum. These bins are also so constructed that the material is thoroughly ventilated. In these bins the calcining is completed, the moisture being driven off by the residual heat of the rock itself. After the gypsum has been partly dehydrated in these bins it is drawn out, crushed, ground, pulverized and bolted.

The retarder is added to the gypsum after this has been finely ground. Usually from 2 to 15 lbs. of the former are required for every ton of plaster. The mixing is done in some form of a mechanical mixer. The Broughton mixer is extensively used for this purpose. An ordinary wall plaster will also contain, in addition to a retarder, a certain per cent of finely picked hair or other fiber, in the proportion of about $1\frac{1}{2}$ to 3 lbs. of hair to a ton of plaster. Wood fiber is sometimes added as a substitute for hair, and such use is growing.

Plaster is usually packed in jute sacks containing 100 lbs., or in paper bags containing 80 lbs. It is customary in the plaster trade, as in the cement trade, to charge for the jute sacks, and give a rebate on the return of the latter. Where the plaster is packed in paper bags, a charge is usually made for these latter.

Flooring plaster and hard-finished plaster are also gypsum products made by burning this mineral until all of its water of crystallization is driven off. Flooring plasters are prepared by simply burning gypsum

at a high temperature, while the hard-finish plasters are produced by a double burning with the intermediate use of some chemical. Practically all of these plasters are imported. Flooring plasters are manufactured by burning pure gypsum, broken into lumps, in a vertical kiln. The kiln is heated by means of a grate, to one side of the kiln, upon which coal is fired. The hot products of combustion pass through, and so heat the gypsum in the kiln. The temperature reached is about 900° F. The time of burning is four hours. These floor plasters give a very hard and durable surface. They must be very carefully used to prevent cracking.

Of the hard plasters, Keene's is the best known, and was originally manufactured under an English patent. This, however, has long since expired. This cement is not only imported into this country, but is also manufactured to some extent here. It is made by burning a very pure gypsum at a red heat. The resulting anhydrous calcium sulphate is immersed in a bath of alum solution and dried, after which it is again burned at a high temperature, finely ground and placed upon the market. It is necessary to employ a very pure gypsum, as the slightest trace of iron would color the cement.

Puzzolan Cements. Puzzolan cements are of very ancient origin, and in most of the engineering work done by the Romans this cement was employed. They manufactured it by mixing slaked lime with fine volcanic ash. These cements are still employed to some extent in Europe, but have never found a market in this country. A cement manufactured from blast furnace slag and slaked lime was made at one time in this country by a number of concerns, but at the present time its manufacture has been almost entirely discontinued. The activity of this class of cements depends upon the fact that the volcanic ash and slag both contain soluble silicic acid, which readily enters into combination with calcium hydrate to form silicates.

In manufacturing slag cement, the cement is chilled and granulated by running it while still molten into water or by directing a stream of water against a stream of melted slag. This slag is then mixed with slaked lime and very finely ground. Slag cement must not be confounded with Portland cement made from slag. Several new forms of slag cement have recently been introduced. These consist in granulating slag of proper composition with water and mixing the slag so obtained with a small percentage of Portland cement clinker. The "Passow Cement," manufactured in Germany, is of this class.

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CHAPTER XI

CLAY, BRICK, AND POTTERY

ALLEN ROGERS

Clays. This term applies to certain natural-occurring, earthy materials which are plastic when wet, but, when heated to a high temperature, become hard and retain the shape of the molded article. Clay is of secondary origin, resulting usually from the weathering of feldspathic rock, like granite. When found overlying the rock from which it has been formed, it is termed primary or residual clay; when washed from the original bed and deposited elsewhere, it is called secondary clay.

Without plasticity, the property that makes clay valuable in manufacture, it would be comparatively useless. Many theories have been advanced to account for this physical property, the most generally accepted being the "*Water of hydration theory*," based upon the relation of plasticity to the amount of hydrated silicate of aluminium present. Among other theories are the "*Plate theory*," "*Interlocking-grain theory*," "*Ball theory*," and "*Colloid theory*."

Classification of Clays. Clays may be classified according to their origin, physical and chemical properties, or uses. Of the several classifications only that of Orton will be given:

High-grade clays (50 per cent or more kaolin with silica)	1. Kaolin 2. China clay 3. Porcelain clay 4. Fire clay (hard) 5. Fire clay (plastic) 6. Potters' clay
Low-grade clays (10 to 70 per cent kaolin with notable percentage of fluxing elements)	1. Argillaceous shale (Paving block) 2. Ferruginous shale (Pressed brick) 3. Siliceous clays (Sewer-pipe and paving brick) 4. Tile clays 5. Brick clays 6. Calcareous shale (Brick)

Kaolin. This group comprises white-burning clays compounded almost wholly of silica, alumina, and chemically combined water, with a slight percentage of fluxing material such as iron. Their formation is principally due to the weathering of pegmatic veins, although in some cases they have originated from granite, quartz, and limestone. When mined they contain a greater or less amount of parent rock, removable by washing. They occur quite widely distributed in the United States east of the Mississippi, but are less important in Missouri, Utah, and Texas. Kaolin is used in the manufacture of white wear, porcelain, tiles, and as a filler for paper.

Ball Clay. These clays are white-burning, but differ from the kaolins in that they are plastic. They find extensive application in the manufacture of white ware, providing the necessary bonding power. They must be as free as possible from iron oxides and possess considerable tensile strength. They occur mostly in Florida, Kentucky, Tennessee, and New Jersey.

Fire Clays. These are capable of withstanding high temperature and owe their refractiveness in most part to the large amount of silica and small amount of fluxing agents they contain. They vary widely in their physical and chemical properties, showing great differences in color, plasticity, texture and tensile strength. They are, as a rule, light in color, ranging from gray to yellowish-red. The deposits may be of either primary or secondary origin and may be divided into plastic and flint clays, the former being plastic when wet, the latter hard and flinty, even when finely ground, but highly refractory. They occur quite widely distributed over the United States. Fire clays are manufactured into fire-bricks, retorts, furnace linings, crucibles, and terra-cotta; while a special grade also adapts itself to the making of pots and tanks for glass manufacture.

Stoneware Clays. These clays differ from fire clays in that they produce a very dense body when heated at a comparatively low temperature. In many instances, however, they are very refractory, but must possess sufficient toughness and plasticity to be worked on the potters' wheel. In making stoneware it is customary to mix clays according to certain characteristics in the finished product. Stoneware clays make stoneware vessels, yellow ware, art ware, earthenware, and even terra-cotta.

Terra-cotta Clays. Clays for making terra cotta differ quite widely, although most manufacturers prefer a semi-fire clay. Buff-burning clays are commonly used, because of the hard body produced on burning. Those suitable for this purpose are found mostly in New Jersey, Pennsylvania, Indiana, and Missouri.

Sewer-pipe Clays. Clays for this purpose are quite similar to those used for paving brick. The easily fluxing clays are of advantage here, because the higher iron content aids in the formation of the salt glaze

that covers the pipes. A small amount of fire clay in the mix retains the shape of the tube during the burning.

Brick Clays. Common brick is usually made from low grade, red-burning clays. The principal requirement is that the clay shall mold readily and burn hard at a comparatively low temperature. Owing to the low market price, poor bricks made from local deposits are often substituted where a better material should have been employed. Pressed brick, on the other hand, calls for a higher grade of clay. The physical requirements here are uniformity of color in burning, freedom from warping and absence from soluble salts, together with sufficient hardness and low absorption when burned at a moderate temperature.

Paving-brick Clays. These clays are made from a large variety of materials, the most common being impure shales, which are widely distributed. They should have a fair degree of plasticity and good tensile strength.

Slip Clays. These contain a large amount of fluxing material, which melts at a low temperature, forming a natural, greenish-brown glaze.

Gumbo Clays. Included in this class are certain fine grained, plastic, and tough clays that cannot be used for brick making, because they shrink on burning. Their chief application is in the manufacture of railroad ballast.

Retort Clays. These dense-burning, plastic, semi-refractory clays, are common in the manufacture of gas and zinc retorts.

Pot Clays. The clays coming under this head are hard-burning and well adapted to the manufacture of pots for glass making.

Ware Clays. These are the same as ball clays.

Pipe Clays. These are similar to sewer-pipe clays.

Sagger Clays. This term applies to clays used in the saggers where high-grade pottery is burned.

Portland Cement Clays. Portland cement is a mixture of lime and clay, either true or shales. (Chapter XIII.)

Paper Clays. In order to give body, weight, and finish to certain grades of paper, some form of clay, plastic and of light color, is mixed with the pulp in the beater engine where it becomes enmeshed.

Paint Clays. Many clays mix well with linseed oil and form a good grade of paint. The color of these clays varies from light yellow to a dark, reddish brown, due to the presence of iron oxide and, in some instances, manganese. The chief clays coming under this heading are the ochers and siennas.

Uses of Clay. To summarize the varied and numerous applications of clays, the table compiled by R. T. Hill and amplified by Heinrich Reis will be given:

"*Domestic.* Porcelain; white ware; stoneware; yellow ware; Rockingham ware for table service and for cooking; majolica stoves; polishing brick; bath brick; fire-kindlers."

"*Structural.* Brick: common, front, pressed, ornamental, hollow, glazed, adobe; terra-cotta; roofing-tile; glazed and encaustic tile; drain tile; paving brick; chimney flues; chimney pots; door-knobs; fireproofing; terra-cotta lumber; copings; fence-posts."

"*Refractories.* Crucibles and other assaying apparatus; gas-retorts; fire-bricks; glass pots and blocks for tank furnaces; saggers; stove and furnace bricks; blocks for fire boxes; tuyeres; cupola bricks; mold linings for steel castings."

"*Engineering.* Puddle; Portland cement; railroad ballast; water conduits; turbine wheels; electrical conduits; road metal."

"*Hygienic.* Urinals, closet bowls, sinks, washtubs, bathtubs, and pitchers; sewer-pipe; ventilating-flues; foundation-blocks; vitrified bricks."

"*Decorative.* Ornamental pottery; terra-cotta; majolica; garden-stands; tombstones."

"*Minor Uses.* Food adulterant; paint fillers; paper filling; electric insulators; pumps; fulling cloth; scouring soap; packing for horses' feet; chemical apparatus; condensing worms; ink-bottles; ultramarine manufacture; emery wheels; playing marbles; battery-cups; pins; stilts and spurs for potters' use; shuttle-eyes and thread-guides; smoking-pipes; umbrella-stands; pedestals; filter-tubes; caster-wheels; pump-wheels; electrical porcelain; foot-rules; plaster; alum."

Building Bricks. Building bricks include common, pressed, glazed and enamel bricks, but as space does not permit a complete description of each, only the manufacture of common building brick will be given. The processes involved may be divided into the preparation of the clays, the molding, the drying, and the burning.

Preparation. Since only a few clays can be used directly as mined, it becomes necessary to subject the material to weathering agencies. This is done by spreading the clay over the ground in a thin layer from 2 to 3 feet deep, and allowing it to remain thus exposed for a considerable period, in some cases a year or more. To hasten the process, however, some clays are disintegrated artificially by means of crushers, edge runners, disintegrators, and roller mills. The grinding is usually done on the dry clay, although sometimes the wet clay is used, and the process is known as tempering.

Ring Pits. These pits are about 25 feet in diameter and from 2 to 3 feet deep. A heavy iron wheel is arranged, by means of gears, so that it travels in the pit and causes a thorough mixing of the mass. The operation lasts from 5 to 6 hours, leaving the clay ready for the brick machine.

Pug Mills. These mills vary in shape and capacity but are all provided with blades to cut up the clay, produce a thorough mixture, and and pass it along to the discharge end. They do not take up as much room as the ring pit and are much more readily handled.

Molding. The simplest form of molding consists in pressing the soft clay or mixture into wooden frames dusted with sand to prevent stick-

ing. This operation, done either by hand or by machine, is known as the *soft-mud process.* In the so-called *stiff-mud process* the clay is tempered with much less water. The prepared clay is forced through a die in the form of a rectangular bar and then cut into brick lengths. The machine for this purpose is provided with an auger screw, which runs in a cylinder that tapers at the end to the size of the die. Dry pressing is sometimes done, as well as semi-dry pressing. In either case, the prepared clay is forced with great pressure into steel molds.

Drying. After molding and before burning, the bricks must be dried. This may be accomplished in several ways, the simplest being to spread the bricks over a smooth flat floor and let them dry in the sun. Pallet driers are covered frames on which the bricks are placed as they come from the machine. Drying in the air has the disadvantage that it is impracticable in cold or damp weather. To overcome this many brickmakers use drying tunnels. The green bricks are placed on cars, run in at the cooler end of the tunnel and gradually pushed along to the warmer end. The tunnels are built in a variety of ways, but when possible the waste heat from other operations is made use of.

Burning. The bricks having been thoroughly dried are placed in kilns and heated to a comparatively high temperature or "burned." The temperature and time of heating depend upon the kind of clay and the degree of hardness desired. The kilns may be either "up-draft" or "down-draft." In the former system the heat from the fire passes into the body of the kiln and up through the ware, finally escaping at the top. The heat in the down-draft kiln enters at the top, passes down over the ware, and escapes through flues at the bottom.

Continuous or ring kilns are also employed. They consist of a series of chambers arranged in the form of a circle, connected with each other and with the stack by means of a series of flues. The fire is built under the chamber that is to receive the highest temperature; from here the heated gases pass to the next chamber, and so on to the freshest charge. In order to utilize the heat from the cooling bricks, after they have reached their maximum temperature, the air supply to the fire is drawn through the chambers containing the thoroughly burned and cooling bricks.

Sewer-pipe Manufacture. Most sewer-pipes are made from shale, which after crushing is mixed with the necessary amount of plastic material and made into the desired shape by a special form of press. The drying and burning is then carried out in a manner somewhat similar that to given for brick.

Hollow Structural Material. Included in this classification are fireproofing terra-cotta lumber, hollow blocks, and hollow bricks. The fireproofing materials are those which are employed in floor arches, partitions, and wall furring for girders and columns. Terra-cotta lumber is a soft and porous material produced by mixing sawdust with the clay

and subsequently burning it out. This being soft can be nailed the same as lumber. Hollow block and hollow brick are used for outside walls.

Fire Bricks. Most of the fire bricks on the market are made from a mixture of several clays to which have been added a certain amount of ground fire brick or quartz. They are made in many shapes and vary greatly in hardness and degree of refractory power. The burning is almost universally conducted in down-draft kilns.

Tile. Under this heading come roofing tile, floor tile and wall tile. They are made in a variety of ways and from a variety of materials. Some are made in a porous condition whereas others are colored and highly glazed.

Pottery. This heading includes a great variety of products ranging from cheap earthenware, such as flower-pots, to the most delicate porcelain vase. In the manufacture of pottery there are certain operations common to all, but with the higher grades much more care and detail are necessarily involved. The general operation consists in the preparation of the raw material, tempering, moulding, drying, biscuit burning, dipping, glost-burning, and decorating.

Stoneware. This class of material is made from low-grade plastic clay, being porous in character, red to cream in color, and glazed or unglazed. Slip-clay, largely used for this purpose, melts to a brown glass at a temperature at which the ware is burned. Salt glazing is a very simple method and is in common use for this kind of ware, although it is applied more especially to sewer-pipe. The articles are placed in the kiln, the maximum temperature reached, and salt thrown into the fire. The high temperature causes a volatilization of the salt which, on coming in contact with the clay, unites with it, forming a glaze on the surface of the ware. In yellow ware the object is burned to develop the body, after which the glaze is applied and the ware heated a second time.

White Ware. Included in this class are those products having a white or nearly white body and usually glazed. Mixtures consisting of kaolin, ball-clay, quartz, and feldspar are the materials which are employed and these are selected with the idea of their white-burning qualities in view.

Porcelain. Prior to the sixteenth century, this term denoted objects made from mother-of-pearl. At the present time, however, the same materials are employed for making porcelain as for white ware. Great care, however, must be exercised in their selection, and the mixtures so proportioned as to give a hard and translucent body. That in which spar is used for the flux is known as hard porcelain and is bluish white by transmitted light, while that fluxed in part with calcium phosphate, known as bone china, is yellow by transmitted light.

Glazes. For all pottery, except hard porcelain, the ware is first

burned in the biscuit kiln, forming porous porcelain, then glazed and burned again in the glost-kiln. The glazes consist of mixtures of acids and bases so combined that they will melt to a glass at the temperature of burning. It is very important also that the coefficient of expansion should agree with the body of the ware, otherwise a defective glaze will be the result.

CHAPTER XII

GLASS

JAMES GILLINDER

Gillinder Brothers, Glass Manufacturers, Port Jervis, N. Y.

Glass is an amorphous product of fusion, differing widely in composition. Ordinarily it is considered as a mixture of an alkaline silicate and the silicate of one or more bases, the alkali being sodium or potassium, the base calcium or lead and sometimes all four elements enter into its composition. While this is true of nearly all commercial glass, it must be noted that at Jena and elsewhere glasses have been made free from alkali, that borates and phosphates have been substituted for silicates, and that many elements such as zinc, barium, magnesium, and antimony have replaced lead and lime, so that it is practically impossible to accurately define glass.

Technically, transparent glasses are divided into lime glass or lead glass according to the presence of these elements. The term flint glass, which originally meant a pure lead potash glass, is now often applied to all clear transparent glass. Sometimes the lime glass is called lime flint. Bottle and window glass are impure forms of lime glass. White or "opal" glass and colored glass are those to which materials have been added to produce the color effect.

There may also be mentioned another class of glasses, which, because of special chemical composition, possess certain chemical and physical properties. Among these are chemical ware, cooking utensils, glass resistant to the passage of x-rays, etc., etc.

H.T. Properties of Glass. The properties of glass are very definitely related to their chemical composition as well as to their "annealing," q.v. The investigations of recent years have given to most of the glass making oxides fixed values, from which, through substitution in formulæ, the various mechanical properties of a glass can be determined.

Specific gravity. If a_1, a_2, a_3 . . . represent the percentage composition of the oxides in a glass, and z_1, z_2, z_3 . . . the values of those oxides for specific gravity, then:

$$\frac{a_1}{z_1}+\frac{a_2}{z_2}+\frac{a_3}{z_3}+\ldots=\frac{100}{s},$$

where s = specific gravity of the glass.

These values for specific gravity of the various oxides are as follows:

SiO_2	2.3	As_2O_3	4.1
B_2O_3	1.9	BaO	7.0
ZnO	5.9	Na_2O	2.6
PbO	9.6	K_2O	2.8
MgO	3.8	CaO	3.3
Al_2O_3	4.1	P_2O_5	2.55

Tensile strength.

$$P = a_1y_1 + a_2y_2 + a_3y_3 + \ . \ . \ .,$$

where P = tensile strength;

$a_1, a_2, a_3 \ . \ . \ .$ = per cent of the various oxides in the glass;

$y_1, y_2, y_3 \ . \ . \ .$ = the values for tensile strength for these various oxides.

Values for tensile strength.

SiO_2	.09	As_2O_3	.03
B_2O_3	.065	BaO	.05
ZnO	.15	Na_2O	.02
PbO	.025	K_2O	.01
MgO	.01	CaO	.20
Al_2O_3	.05	P_2O_5	.075

Coefficient of Expansion. This is one of the most important factors in a glass, to withstand sudden temperature changes.

$$3\alpha = a_1y_1, \ + a_2y_2 + a_3y_3 + \ . \ . \ .$$

where $\frac{3\alpha}{10^7}$ = coefficient of cubical expansion;

$a_1, a_2, a_3 \ . \ . \ .$ = per cent of the various oxides in the glass;

$y_1, y_2, y_3 \ . \ . \ .$ = values for the various oxides.

B_2O_3	.01	BaO	3.0
MgO	.01	PbO	3.0
SiO_2	.8	CaO	5.0
ZnO	1.8	Al_2O_3	5.0
P_2O_5	2.0	K_2O	8.5
As_2O_3	2.0	Na_2O	10.0

Resistance to temperature changes is dependent upon the various mechanical and thermal properties.

This resistance is greater:

the greater the tensile strength P;
the less the coefficient of expansion α;
the less the resistance against elastic change E;
the greater the heat conductivity k;
the less the specific heat c;
the smaller the specific gravity s.

The coefficient of resistance may be expressed by the equation

$$F = \frac{P}{\alpha E}\sqrt{\frac{k}{s \cdot c}}.$$

For further data on the relation of properties to chemical composition see Hoestadt "Jena Glass" and Dralle "Die Glasfabrikation."

The following are the chief raw materials used in making glass:

Silica. Silica is usually introduced in the form of sand, which may vary in purity, according to the source and care in preparation. The chief impurities in sand are iron, alumina and organic matter. The presence of a small amount of alumina does not injure the glass, but iron acts as a coloring agent, producing a green of more or less intensity, depending on the quantity present and the state of oxidation. For the finer glass, therefore, a sand as free from iron as possible is required, while for more common ware, such as green bottles, a much larger quantity is permissible. Sand from Berkshire, Mass., is practically free from iron, while that from Pennsylvania and West Virginia often contains less than one-tenth of one per cent. Sand from New Jersey usually has a much higher iron content.

The sand must be of uniform size, not too coarse to prevent reaction with the other material, nor yet so fine as to cause the reaction to take place too violently and cause excessive foaming during the melting. Natural silicates, such as feldspar, are sometimes used as a source of silica, because of the alumina and alkali which they contain. Slags from metallurgical processes have been used for common ware with varying success.

Alkali Metals. *Sodium carbonate* (soda ash) is the chief source of soda and is obtained from the trade in a pure condition. *Sodium sulphate* (salt cake), owing to its cheapness, is also used in the manufacture of plate and window glass. Its use requires the addition of carbon as a reducing agent and is attended with many difficulties not met with when the carbonate is used. The amount of carbon added is much less than that called for by theory and it is impossible to give an exact explanation of the reaction. *Sodium nitrate* (Chile saltpeter), either as it comes from Chile (95 per cent) or refined for the better ware, is used as an oxidizing material to destroy organic matter and to change the iron to the ferric condition. *Potassium carbonate* (pearl ash, potash, salts of tartar)

usually hydrated, containing from 80 to 85 per cent potassium carbonate, is the chief source of potassium in the glass industry, sulphates and chlorides being the chief impurities. In some European factories crude pearl ash from the sugar refineries is used in the cheaper kinds of glass. *Potassium nitrate* is also used as an oxidizing material.

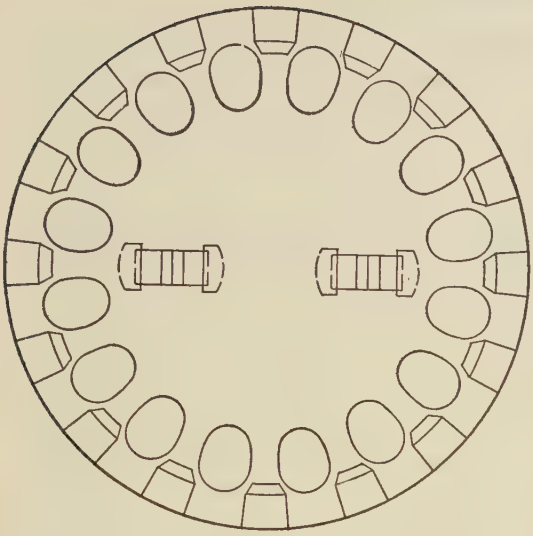
Alkali Earths. *Calcium* is introduced as a carbonate or oxide. Limestone occurs in nature of sufficient purity for use after simply grinding. The advantage of the different forms of lime is an open question, some works preferring one, some another. The advantage of burnt lime is the saving in heat by the removal of the carbon dioxide before entering the furnace, while on the other hand the liberation of carbon dioxide from the carbonate helps stir the glass during the melting process. Iron in all glass-making materials is harmful where crystal clearness is required, while magnesia makes the glass hard and more difficult to "plain," though many American factories use a lime high in magnesia content without any apparent disadvantage. *Barium* is sometimes used in the form of sulphate together with carbon, but more generally as a carbonate either natural or prepared. It produces a glass high in refractive power and is used for many optical purposes.

Heavy Metals and Acid Radicals. *Lead* is used generally as red oxide or litharge to impart brilliancy and to produce glass of high refractive power. Red lead, because of the oxygen which it liberates, is preferred to litharge. Freedom from metallic lead and discoloring metallic impurities, such as copper and iron, is required. *Zinc* is used as oxide to replace lime or lead, especially in the modern heat-resisting glasses. It is also largely used in opal glass. *Boric acid* and *borax* are used in optical and heat-resisting glass as well as in colored glasses. *Phosphate of lime,* bone ash, is used to produce opalescence or opacity depending upon the quantity. Bone ash, unless it is present in large quantity, requires "reheating" to bring out the opalescence. *Feldspar* is used as a source of alkalies and alumina. Used with fluorspar it produces opal glass. *Fluorspar* used with feldspar or alumina produces opal glass. Iron and metallic sulphides (lead and zinc) are the chief harmful impurities. *Cryolite, sodium aluminium fluoride,* used alone, produces dense opaque glass, but owing to its solvent action on the clay pots other materials are taking its place. It is largely used in making opal glass by the tank method. *Arsenic* as white oxide is used in opalescent and opal glass and in enamels. *Tin oxide* is used to a limited extent in colored glasses and in enamels. *Antimony* as oxide, sulphide or metal is used in colored glasses and the sulphide is employed in tank glass to "improve the color."

Coloring Materials. *Uranium,* usually as sodium uranate, is used to produce a peculiar yellow fluorescent glass. When in the ferrous state, *iron* colors glass green, and yellow when in the ferric condition. The temperature of the furnace, however, materially affects the state of oxidation of the iron, a high temperature changing it from yellow to green (see

manganese). As a colorant it is usually added as red oxide or iron scales. *Chromium* produces green and greenish-yellow glass. The oxide Cr_2O_3 is very hard to dissolve; hence potassium dichromate or other metallic chromates are used. *Manganese.* Black oxide, MnO_2, is the most used of all the coloring oxides. In large quantities it produces black, and in less amount purple to light pink color. It is used to correct the color effect of iron, which is always more or less present in glass material. It acts as an oxidizing agent also. The quantity of manganese to be used depends on the amount of iron present and the temperature of the furnace, as the hotter the furnace the more manganese is required. The heat "burns out the color." (See under Iron.) The impurities met with are iron and earthy matter, while cobalt is sometimes present in sufficient quantities to be harmful. *Nickel,* as oxide, is used in a very limited way. European practice substitutes it for manganese in some glasses, but American factories have not found this satisfactory. *Cobalt,* as oxide or smalt, is employed in giving an intense blue color. The blue from cobalt shows purple by transmitted light. *Gold* as chloride or purple of Cassius, is used to produce a ruby color. *Copper* in the cuprous form produces red, in the cupric it produces a peacock-blue color. *Selenium* is used to produce a red color. It is also used as a decolorizer. *Cadmium sulphide* forms a lemon yellow color in lead-free glass. *Carbon* is used as a reducing agent in sulphate glass. In the form of coke, oats, bark, and other organic matter it produces an amber color in lime glass.

Pot Furnaces. Furnaces in which the glass is melted in clay crucibles or pots are known as pot furnaces, while those in which the glass is melted in one large rectangular clay tank are known as tank furnaces or tanks. Pot furnaces are either open or closed, and may be fired either direct, regenerative or recuperative. Tanks are either "day" or continuous, working either intermittently or continuously. The direct fired coal furnace is still used, but the regenerative furnace (see Fig. 145) is the most satisfactory and economical of pot furnaces. In this type the burnt gases from the furnace are made to pass through fire brick checker-work flues which then become highly heated. The direction of the draft is then reversed by suitable dampers, and the incoming air and gas (see Chapter on Producer Gas) are led through; while the burnt furnace gases go to heat another checker work which has become cooled by the incoming air and gas of the previous run. Thus the burnt furnace gases give up their waste heat to the checker work, which in turn gives it up to the incoming gas and air. In practice this reversal of draft is made every twenty or thirty minutes. In the recuperative furnace there is no reversal of draft, but the hot burnt gases pass through clay tubes which by conduction give up their heat to the incoming air and gas. This furnace is used abroad, but has not been adopted widely in America.



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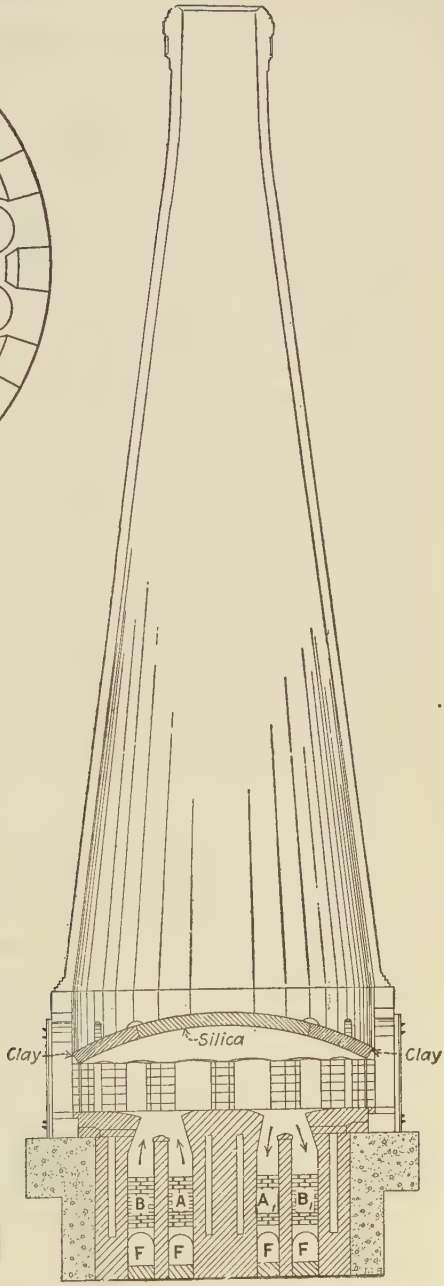

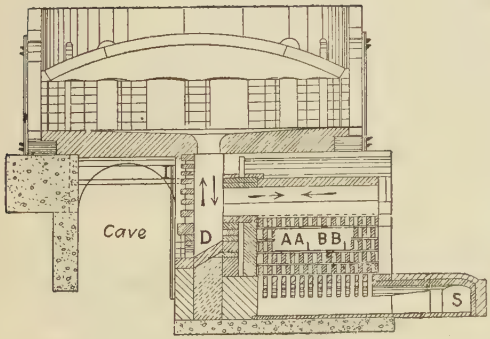

B FIG. 145. A

A—Showing vertical section through a regenerative pot furnace, AA_1, BB_1, checker work; *F*, flues for gas and air. The high chimney is not necessary but is usually built for factory ventilation.

B—Showing the position of the regenerators and the "cave" where glass from broken pots can be removed at *D*. The flues *S* lead to the reversing valves and to the draft stack (not shown in illustration).

C—Horizontal section showing position of pots.

Tank Furnace. The introduction of the tank furnace marked an epoch in the glass industry. The batch is put in a shallow fireclay tank covered with a refractory arch of silica brick and heat applied to the surface of the batch. The simplest form is the intermittent or "Day Tank." The batch is shoveled in, the work holes are closed and heat is applied, either oil or gas being used. When the glass is "plain" the heat is reduced, the work holes opened, and when cooled sufficiently the glass is worked. These tanks are filled in the afternoon and are ready to work the following morning, hence the name. To obviate the loss of heat by this method continuous tanks are used. These are usually much larger than the day tanks and are usually divided into compartments by fireclay obstructions. The batch is filled in at one end of the tank, Figs. 146, 147 and 148, and after melting flows under the obstruction to the working end. As fast as the glass is worked out, a new batch is introduced so that the melting and working go on continuously, thus maintaining a nearly constant level of glass. The continuous tank is the most economical form of glass furnace, and wherever large quantities of glass are made, it is used. The glass produced is not so good in color as that made in closed pots, so that for the finest ware or where small quantities are made, pot furnaces are still employed.

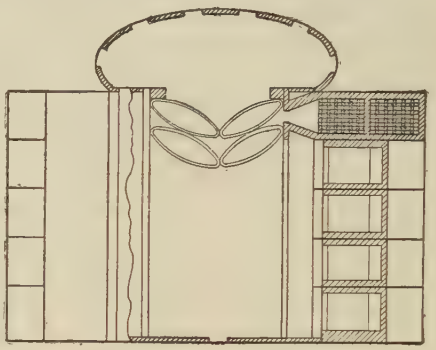

FIG. 146.

Horizontal section showing where batch is fed in, and clay obstructions known as floaters under which the glass must flow to reach the working end.

The air and gas passing through the hot checker-work A, B, burn, pass through the melting compartment and out to the stack, giving up their residual heat to the checker-work A_2, B_2. In about twenty minutes, when A and B have become cool and A_2 B_2 hot, the direction of the draft is reversed. By such reversals a minimum of heat is lost and a maximum temperature maintained.

The temperature of the glass furnace is indicated by means of pyrometers chiefly of the thermo-electric type. A temperature of 1400–1500° C. is usually maintained in pot furnaces, while in tanks the temperature runs somewhat higher. It is not safe to run much above this, owing to the danger of melting the pots and the furnace materials.

Melting Pots. These are of two kinds—open and covered. The covered pots are used in making flint glass, the open ones, which are now chiefly used in the manufacture of plate and optical glass. The manufacture and handling of glass pots require great care (see illustrations). The

fireclay is carefully mixed with ground burnt clay or old potshell, and after moistening is worked into a doughy mass (pugging). Men than tramp this mixture with bare feet to increase its plasticity, and after several months of aging it is ready for use. The bottom of the pot is first formed by making a layer of clay 4 or 5 ins. thick, then the sides are built up a few inches at a time, the clay being worked by hand into the already built-up part, Figs. 150–156. When not being built they are covered with damp cloths to keep the clay moist. After the pot is finished it is allowed to dry in a warm room of constant temperature, and away from drafts. After several months the pot is

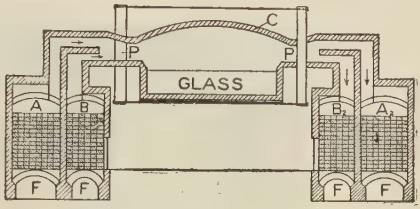

FIG. 147.—Continuous Tank.

F = flues for gas and air;
A, A_2 = air checker work;
B, B_2 = gas checker work;
P = ports for entrance and exit of gas and air;
C = silica brick arch.

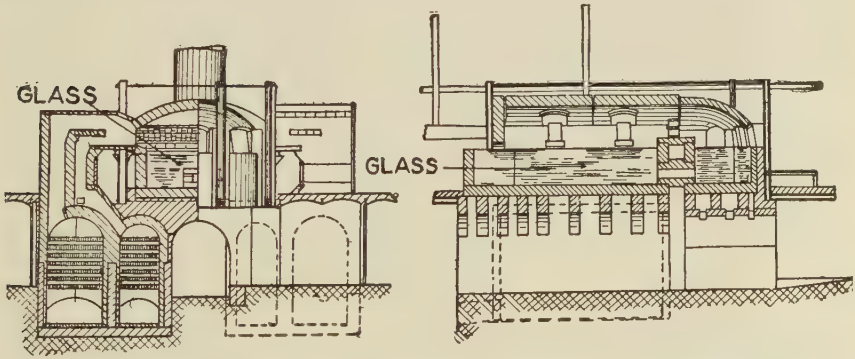

FIG. 148.*—A Type of Continuous Tank, showing another form of obstruction—a wall with an opening at the bottom through which the glass flows to the working end.

ready for use; but before it can be placed in the stack it must be gradually raised to the temperature of the furnace. This preliminary heating is done in an auxiliary furnace known as a pot arch, Fig. 157. Having been raised to a white heat the pot is transferred to the place in the furnace made vacant by a broken pot. This operation is known as "pot setting." Before using, the pot is glazed with molten glass to retard the action of the batch upon it.

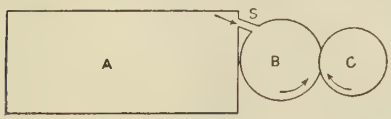

FIG. 149.—Diagrammatic representation of an Owens' unit.

A = Continuous melting tank;
S = Discharge spout;
B = Revolving working tank;
C = Owens' machine.

Pots vary in size from those holding but a few pounds (known as monkeys) to those holding several tons. The life of a pot varies greatly. It may be broken from the outside by a sudden change of temperature, or by one of many other causes, but the natural end of a pot is by cor-

rosion from the inside. This corrosion varies with the different kind of batches. Some pots may last but a few weeks, while others may remain

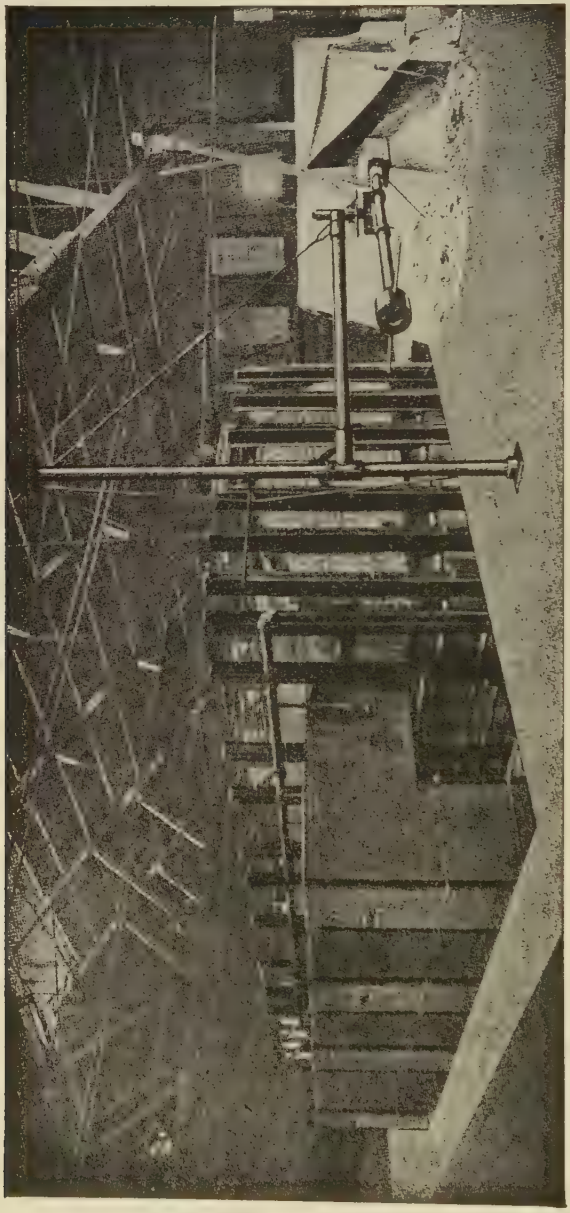

Fig. 149*a*.—Exterior of Continuous Tank, showing side ports and filling end.

perfectly good for a year. Sometimes a pot is taken out before it breaks because it is introducing small pieces of clay (stones) into the glass.

Melting Process. The batch, made by weighing and carefully mixing the various materials together with some broken glass (cullet), is filled into

the pot and the stoppers luted on. In the best practice the cullet is crushed before mixing and separated from stray iron by a magnetic separator. After this charge has melted more material is added until the pot is full; usually one such "topping" is sufficient to do this, but sometimes it must be repeated. Some factories do not top excepting over Sunday, but get the glass quicker during the week with "one filling." Test pieces (proofs) are taken out from time to time on the end of an iron hook. The glass at first shows opaqueness, gradually becoming vitreous and transparent, but full of small bubbles (seed). As the melting proceeds, however, these bubbles become fewer and larger and finally when they have all "gone off"

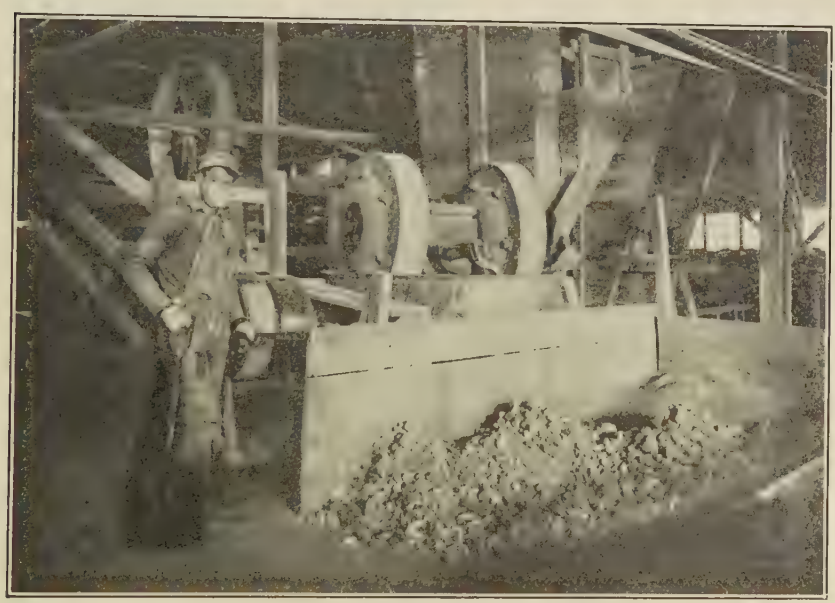

Fig. 150.—Potmaking—Grinding Burnt Clay.

the pot is "plain" and ready to "take down." The stoppers are now removed and the pot allowed to cool, either naturally or by blowing air into it. The dirt and impurities are removed from the surface and the glass or "metal," as it is called, is ready to work. The ordinary practice is to work a covered pot every other day, but where the pots are not topped or the furnace is very hot they may be worked oftener. No definite time, however, can be given for the length of melting, as it varies with the size and thickness of the pot, the kind of glass being melted and the temperature of the furnace.

The reactions taking place in a glass furnace cannot be given with any degree of accuracy, but the process of the fusion is the union of the bases and silica to form mixed silicates with the liberation of carbon dioxide and in some cases oxygen, sulphur dioxide or other gases.

Among the defects of glass are the following:

Seedy. Containing small bubbles of unexpelled gas. This is caused usually by too low a temperature or not sufficient time in melting. Some glasses (especially optical glass containing barium) are impossible to "plain."

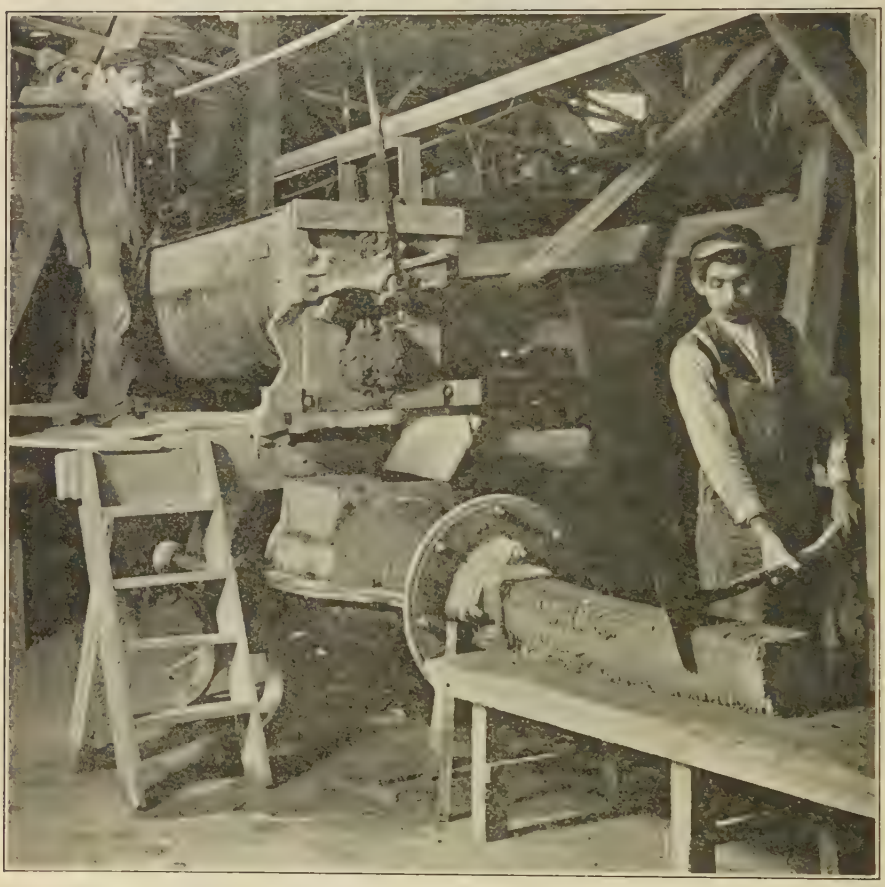

Fig. 151.—Potmaking—Pugging Pot Clay.

Stony. Containing undissolved portions of batch or small particles of clay from the walls of the pot or tank.

Cordy, wavy. The glass not being perfectly clear, but having threads of more or less sharpness running through it.

Sandy. Caused by the separating out of small crystals (Devitrification.)

High Color. Pink from excess of manganese.

Low Color. Green from excess of iron.

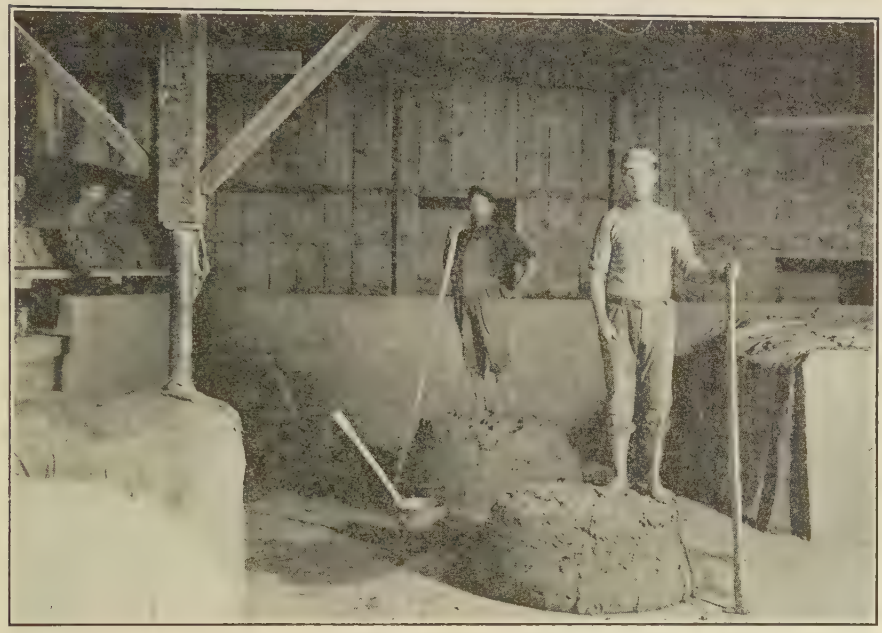

FIG. 152.—Potmaking—Tramping Pot Clay.

FIG. 153.—Potmaking—Transferring Pot Bottom to Working Bench.

FIG. 154.—Potmaking—Building Sides.

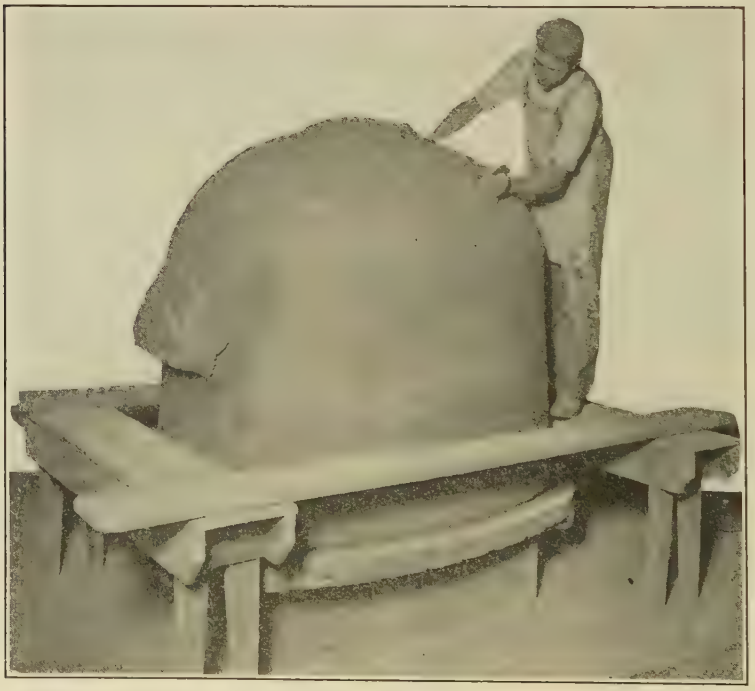

FIG. 155.—Potmaking—Closing in Top.

In many glasses no attempt is made to destroy the green color due to iron.

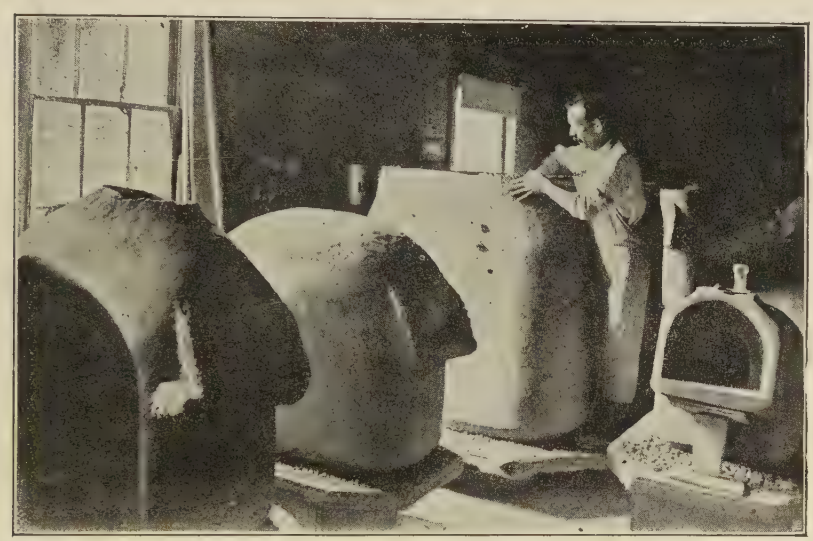

FIG. 156.—Making Pots, showing how the clay is worked in by hand and monkey pots in various stages of manufacture.

Processes of Manufacture. The working of glass depends upon the fact that it passes from a liquid to a solid state without crystallization

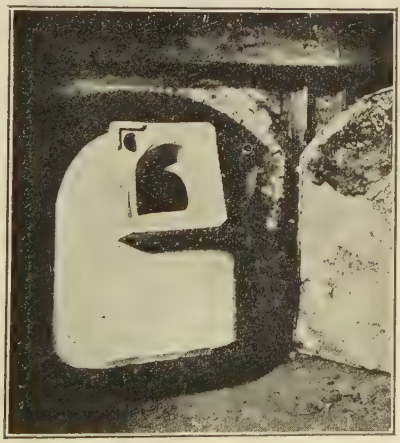

FIG. 157.—Covered Pot, showing pot arch. This pot weighs about 3000 lbs. and will hold two tons of batch.

and possesses, when in a hot condition, ductility and malleability to an extreme degree.

Casting. Plate glass is made in open pots that can be removed from the furnace and their contents poured on a casting table and then rolled to the desired thickness by a metal roller. (Figs. 158–159.) The plate of cast glass is then transferred to a kiln or annealing oven (lehr) and gradually allowed to cool. After the plate, which is rough and uneven, is cooled, it is fastened to a table with plaster of Paris, ground with revolving iron rubbers and sand, first coarse, then finer until the surface is even and smooth. It is then polished by felt-covered rubbers and rouge paste. The plate is then reversed and the other side ground and polished.

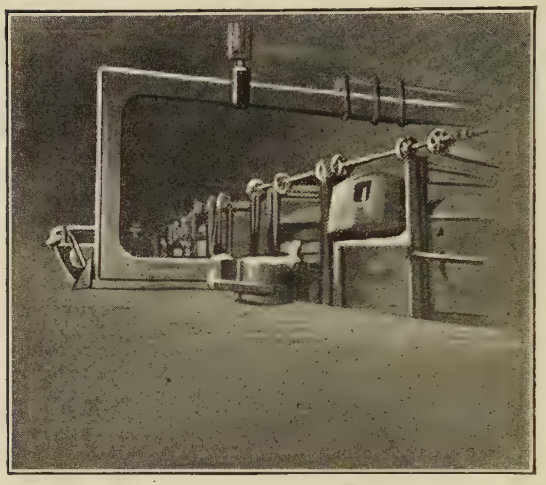

FIG. 158 *—Removing a Pot of Plate Glass from the Melting Furnace to the Casting Table.

Unpolished plate glass, known as rough plate, is made similar to regular plate glass excepting that the glass is taken from the pot in large steel ladles and poured on a table between guides. The table or the roller often have a design on them, thus producing ornamental effects in the glass.

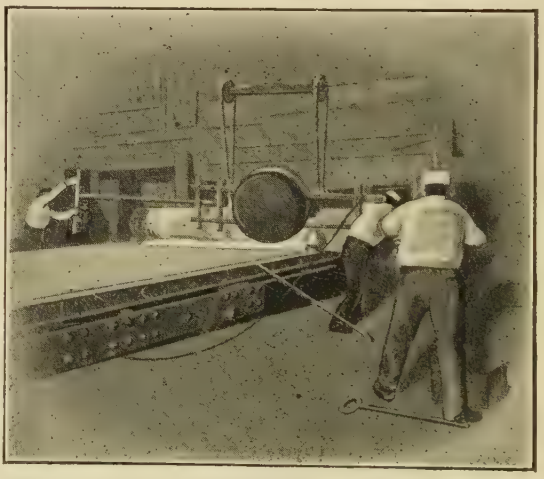

FIG. 159.*—Casting Plate Glass.

Wire glass is rolled plate in which wire has been imbedded during the rolling process. Special care is necessary to prevent this glass from flying apart owing to unequal expansion of the

* Cuts loaned by H. L. Dixon Co., Pittsburgh.

glass and wire. Polished plate glass of opal and black glass have been made and used for table tops, sanitary wall, and for other purposes.

Pressing. Glass is gathered on the end of an iron rod (punty) by revolving it rapidly in the molten glass. It is then carried to the workman (presser), who cuts off with shears the amount desired and allows it to drop into the mould. A metal plunger is then forced into the mould and forces the glass to fill the space between the plunger and the mould. Fig. 161. When the glass has become firm, the plunger is withdrawn, the mould opened and the article either sent direct to the annealing oven or first reheated in an auxiliary furnace (glory hole) to remove mould marks or to alter the shape.

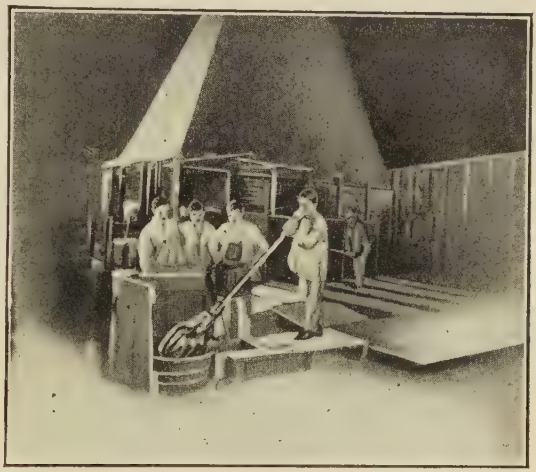

Fig. 160.*—Starting a Cylinder of Window Glass.

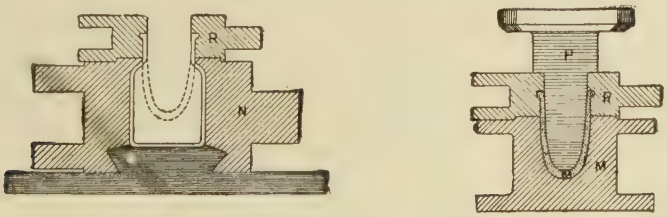

Fig. 161.*—Moulds for Pressing and Blowing a Bottle.
M=press mould; R=ring; P=plunger; N=blow mold; G=glass.

Press moulds are made of cast iron and so constructed that the pressed article can be easily removed. The temperature of the mould and plunger is regulated by streams of air blown against them, the expansion and contraction of the mould being carefully controlled by the workman. The plunger is usually operated by hand power, but for many purposes compressed air is used.

Blowing. Window glass until recently was entirely hand made, but machines are being introduced which are replacing hand labor. In the hand-made glass the workman gathers a lump of glass on the end of a hollow iron pipe and after cooling it a little, introduces it into the molten

glass and gathers more. This is repeated until he has sufficient for his purpose. Then by blowing and swinging and further manipulation (Fig. 162), he produces a large cylinder of glass. The surplus glass is cracked off the ends of the cylinder and it is cracked lengthwise for the next operation. Fig. 163. The cylinder is then gradually heated in a flattening oven and as it begins to soften it is flattened by rubbing on a flat stone, after which it is transferred to the annealing oven and gradually withdrawn from the heat.

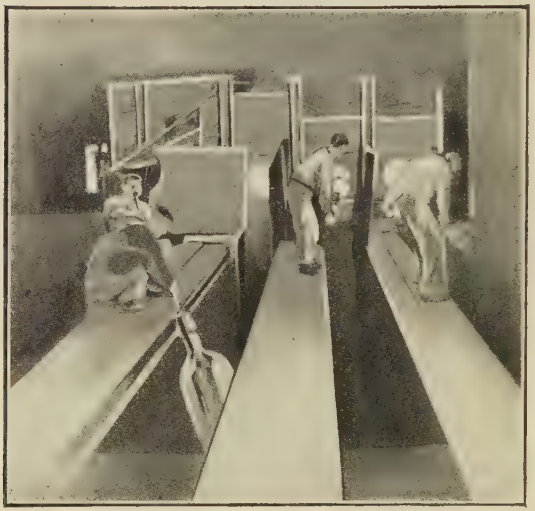

FIG. 162.*—Blowing Window Glass.

Window glass is now generally made in continuous tanks, which have replaced the old open-pot furnaces.

Machine-made window glass is made by immersing a blowpipe in molten glass, introducing compressed air and gradually withdrawing the blowpipe from the molten glass. By carefully regulating the speed of withdrawal and the amount of air introduced cylinders of any length are made and flattened as usual.

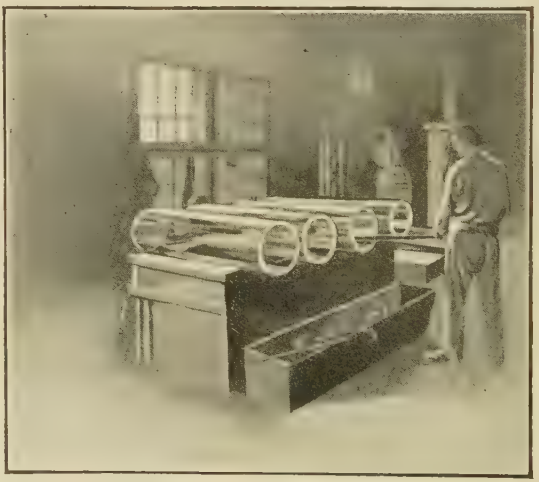

FIG. 163.*—Splitting a Cylinder of Window Glass Preparatory to Flattening.

Another process which has not passed the experimental stage is to replace the blowpipe by a flat bar and passing over rollers into a continuous lehr produce a continuous sheet which is cut off and selected as it comes from the lehr.

Crown Glass. Crown glass, once the chief source of sheet glass, is now made only for special purposes, such as microscope slides and cover glasses, where a surface free from imperfections is required. It is made by blowing a ball of glass, attaching to the side away from the gathering iron a hot iron rod (punty) and cracking it off the gathering iron. The glass is then heated and rapidly revolved until it forms a large flat disk, when it is annealed and selected.

Hollow Ware. Hollow ware is shaped in moulds of metal or wood. The glass is gathered on a hollow pipe, and after shaping by rolling on a polished plate (marver) or revolving in a hollow iron or wooden block it is blown into the mould and takes its shape. Fig. 164.

In the case of chimneys, tumblers and other cylindrical articles the glass is revolved in the mould and shows no joint or mould mark. Such moulds are lined with charcoal or special paste which enables the glass to be turned. In the case of lantern globes or articles with raised or sunken patterns the glass is blown without turning and takes the exact impression of the mould (iron mould).

Fig. 164.*—Blowing Lantern Globes.

Bottles. Bottles are made by blowing in a mould, and after reheating the neck is finished with a special tool.

The recent advances that have been made in the making of bottles, fruit jars, etc., combine pressing and blowing. A blank is pressed in a mould having the shape of the neck and with a weight of glass sufficient to make the bottle. This blank is then removed by means of a ring and placed in a mould the shape of the finished bottle and blown to shape by compressed air. Fig. 165. In some machines a gatherer and presser are required, in others only a gatherer, while in some the glass is flowed through a spout to the machine.

The Owens Automatic Machine works on a different principle from the pressing and blowing machine, as it sucks the glass into the neck forming mould and then blows it to shape in the bottle mould. Fig. 166.

The glass is melted in the continuous tank *A* and flows into the working tank *B* through the discharge spout *S*, Fig. 149. As the arms carrying

the blank moulds, Fig. 167, of the revolving machine, Fig. 166, pass over the surface of the glass in the working tank *B* they are depressed and by the forming of a vacuum, glass is sucked into the blank mould. Fig. 168.

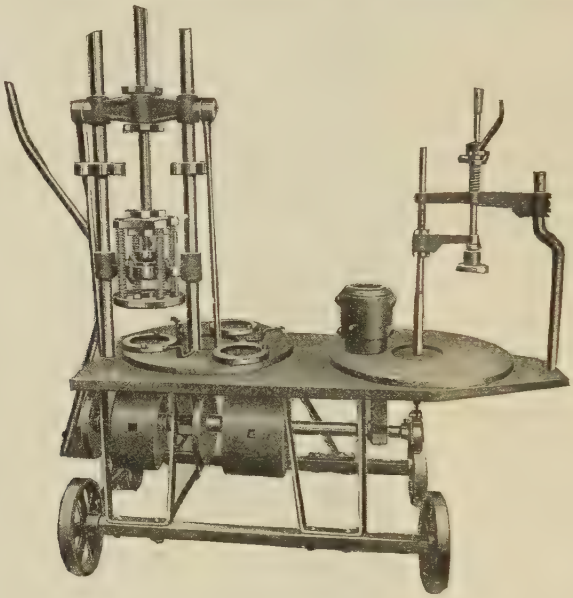

Fig. 165.—Pressing and Blowing Machine. On the left the press; on the right the device for blowing with compressed air. See Fig. 161.

As the mould nears the edge of the tank it is raised and the surplus glass is cut off (Fig. 169) by the shears which also form a bottom for the blank mould (Fig. 170).

Drawing of Owens bottle machine showing (on the left) the blank mould sucking up molten glass and the bottle mould out of its blowing position. On the right it is shown in its blowing position.

When the glass has chilled a little the blank mould opens and there is brought around the blank the bottle mould (Fig. 171).

Compressed air is then introduced and the glass is blown to the shape of the mould (Fig. 172).

When the glass has chilled sufficiently to be handled the bottle mould opens (Fig. 173) and the machine delivers the bottle ready to be taken to the annealing lehrs.

Each machine has eight or more arms and by regulation of the temperature of the molten glass and the moulds, bottles are produced with great uniformity and speed. Machines turning out forty and even more bottles per minute are now in operation.

The introduction of this machine has revolutionized the glass industry and bottles are now produced in plants where the entire process from the mixing of the batch to the annealing of the finished bottle is done automatically.

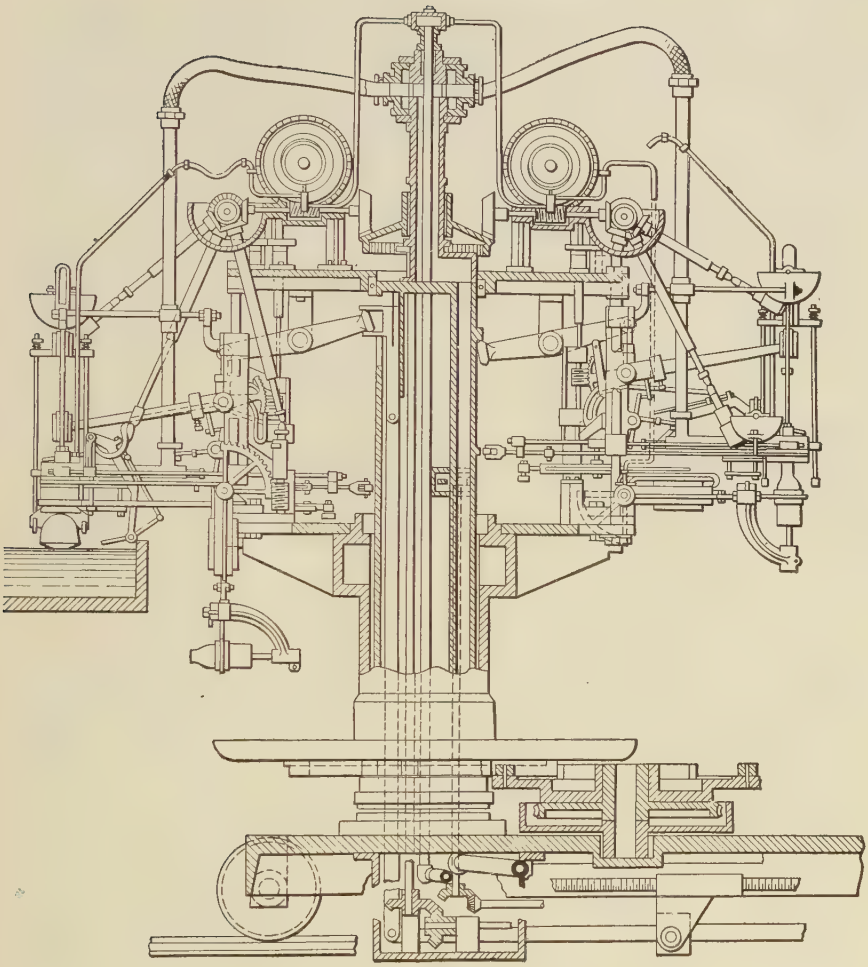

FIG. 166.

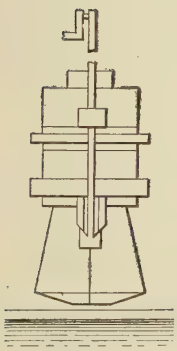

FIG. 167.

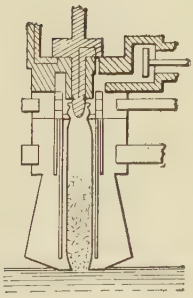

FIG. 168.

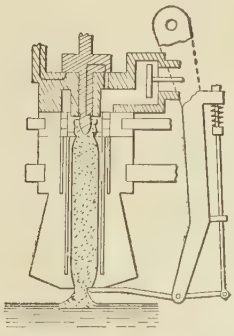

FIG. 169.

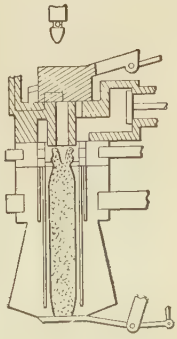

FIG. 170.

Large objects such as vats, jars and even bathtubs have been made by the Sievert process. Molten glass is cast on a perforated metal table and after being properly distributed the chilled edges of the glass are clamped and the table turned over. The hot glass sags and is then blown into shape by compressed air. A mould or other form is used to give the desired shape.

Optical Glass. Optical glass is usually made in a one-pot furnace and differs from other glass in being allowed to remain in the pot until it has become cool. The batch is melted and after it has become "plain" is stirred with a burnt fire-clay rod to produce uniformity and

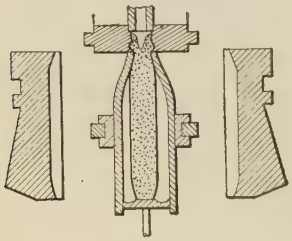

Fig. 171.

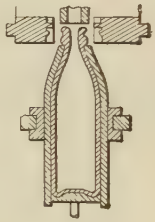

Fig. 172.

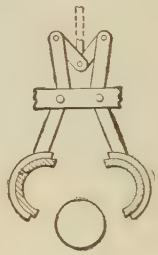

Fig. 173.

destroy stria. Then the glass is quickly cooled until it loses its fluidity, and after this it is very gradually cooled. When cool the pot is broken open and the glass sorted. Only a small portion is fit for use. In recent times advances have been made in this kind of glass, especially at Jena, where many of the optical glasses have originated.

At the present time a large quantity of optical glass is made in furnaces containing many pots. After the glass in the pots is homogeneous and ready to cool, the pot is either transferred to a cooling furnace or the glass is poured like plate glass (q.v.) and carefully annealed. These plates are then cut into sections the desired size and ground and polished. Sometimes in order to produce certain shapes these flat sheets are placed over forms and brought to a temperature sufficient to soften the glass and compel it to assume the shape of the form. This is done in the case of reflectors. Optical glass is now being made in large quantities in the United States.

Annealing. In all the processes of manufacture, with but a few exceptions, the finished articles while still hot are taken to an oven and gradually cooled. If glass is cooled suddenly it develops great internal strain so that it is likely to fall to pieces under change of temperature or when its surface is scratched. An extreme case of sudden cooling is the Prince Rupert drop, a piece of glass produced by dropping a bit of molten glass into cold water. Instead of flying to pieces it becomes very hard and tough, but if scratched with a file or its thin tail broken the drop flies into a fine powder. Glass possessing internal strain is readily detected under polarized light.

To obtain glass free from strain it must be "annealed" or cooled gradually. This is accomplished either by placing the finished article in a heated room and allowing the fire gradually to die out (kilns or ovens) or by gradually withdrawing the article from the heat (lehrs). The former method is used for heavy articles such as carboys, plate glass, blanks for cutting, and optical glass, while the continuous lehr is used for lighter ware. Recently, however, such improvements have been made in continuous lehrs that large articles and even plate glass can be successfully annealed in them.

In most lehrs the gases from the fuel come in contact with the ware to be annealed but the best practice in many cases now calls for muffle lehrs where the glass passes through a heated muffle and does not come in contact with the products of combustion.

The time of annealing varies from a few hours in the lehrs to a week or more in the kilns, depending on the thickness and composition of the glass. In annealing optical glass the cooling is carefully controlled and of long duration, as any sign of internal strain renders it unfit for use.

Colored Glass. *Amber* is produced by the addition of carbonaceous matter, e.g., grain, coke, coal, sawdust, or other organic matter, to a lime glass. The intensity and shade of color depend on the kind and quantity of matter added. Amber is also produced by sulphur and certain sulphides. *Black* is produced by an excess of coloring matter such as manganese, cobalt, or iron. *Blue* can be produced by cobalt or copper. When produced by cobalt it is dark, showing purple by transmitted light. The copper blue is a less intense color, bordering, on the green. *Canary*, a special color produced by uranium. See yellow. *Green.* Chromium or iron alone will produce a green glass, though it is usually made by combining several oxides, such as copper and iron or chromium and copper. *Gray*, "London Smoke." When substances producing complementary colors are added to the same glass a gray color is produced. *Opalescent.* Glass resembling the opal is produced by the addition of arsenious oxide and calcium phosphate. When this glass comes from the pot it is colorless, but on allowing it to cool and then reheating, the opalescence is developed. If the cooling is carried too far the opalescence is lost and a milky effect produced. Opal or white opaque glass was originally produced by the addition of cryolite or an excess of calcium phosphate (bone ash). Mixtures of fluorspar and minerals containing aluminium, such as feldspar, have been substituted and recently artificial compounds bearing fluorine, such as aluminuim fluoride, and sodium silico fluoride, have been used. *Purple* is produced by manganese dioxide. *Red* or *Ruby* is produced by gold, selenium or copper. In the use of copper great care is required to have the copper in the right condition of division and reduction. The glass, as it comes from the pot, is usually light green in color but on cooling and reheating an intense red (such as is used for

railroad signal lights), is produced. The color, however, is usually too intense for use alone so it is "flashed" by gathering a small quantity of the ruby glass and then covering it with sufficient clear glass to make the desired color. "Flashing" is frequently resorted to in making colored sheet glass. Gold ruby is worked very much the same as copper ruby, excepting it can be produced sufficiently light in color to be used alone, though flashing is often used to reduce the intensity. Gold ruby as it comes from the pot is colorless or yellow, but when properly cooled and reheated develops the ruby color.

Selenium ruby is now made which requires no reheating or flashing. It is chiefly used for signal purposes.

The cause of the peculiar action of these and some other glasses has recently been discovered by the researches of Siedentoff and Szigmondi on ultra microscopic particles. They have shown that the metallic gold or cuprous oxide exists in an extremely fine state of division probably held in a mechanical suspension resembling a colloidal solution. Thus it is that if the gold or copper remain in solution, as when they come from the pot, the red color is not produced, but if the correct manipulation of the glass takes place the colloidal solution is produced and the red coloration results.

Artificial gems are highly refractive glasses of purest materials and colored with metallic oxides to imitate precious stones. The colorless glass is known as strass. These glasses are usually soft, because of the large quantity of lead used to produce the high refractivity.

Finishing Processes. Decorated or painted glass is produced by painting on the glass with easily fusible glazes. These glazes are finely ground, mixed with oil and applied to the object and after drying it is put in a kiln and heated sufficiently to fuse the glazes. Cut glass is usually a highly refractive lead glass which when cut shows a beautiful play of prismatic color. The design is first marked out with red paint and then "roughed" with sand or carborundum on an iron wheel. It is then "smoothed" on a fine-grained stone wheel and finally polished on a

APPROXIMATE COMPOSITIONS OF VARIOUS KINDS OF GLASS

	Plate.	Window.	Lime Flint.	Lead Flint.
SiO_2	71	71	74	54
PbO	.....	.....	.....	35
CaO	13	11	7	
Na_2O	14	15	19	
K_2O	.....	.....	.....	11
Al_2O_3, Fe_2O_3	1–2	1–2		

The iron and aluminum vary with the purity of the materials.

wood wheel with putty and pumice. Of recent years this last operation has been replaced by dipping in strong hydrofluoric acid. Glass is obscured or roughed by means of sand blast or by dipping in a bath of alkaline fluorides.

In etching designs on glass a print is made on paper, using a protective wax as ink. This print is transferred by rubbing it upon the glass. The paper is removed, leaving the ink design on the glass. The inside of the article is now protected by wax and then immersed in hydrofluoric acid. The acid etches the part exposed, but does not affect the parts protected by the ink or wax. The wax is then removed by hot water, leaving the finished design. Often the glass is first obscured by the sand blast and the design etched in the roughened surface.

ANALYSIS OF JENA CHEMICAL WARE GLASS

Comp. rend. 163; 355–7 (1916)

SiO_2	66.04	MnO	.40
B_2O_3	8.02	ZnO	10.02
P_2O_2	.03	MgO	5.98
Al_2O_3	1.05	Na_2O	8.14
FeO	.38		

APPROXIMATE BATCHES FOR GLASS

Plate Glass.		*Lime Glass.*		*Lead Glass.*	
Sand	100	Sand	100	Sand	100
Soda ash	30	Soda ash	35	Potassium carbonate	35
Limestone	30	Lime	12	Red lead	60
		Nitre	10	Nitre	10

Cullet is added to the above batches in varying proportions.

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CHAPTER XIII

WHITE LEAD

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The name white lead applies to a compound consisting of carbonate of lead and hydrate of lead in chemical union. It is a commercial name, and is distinctive of a definite product which has been upon the market for hundreds of years. During the year 1907, about 130,000 tons of white lead, were manufactured in the United States. This amount, produced in a single year, exceeds the total amount of all straight pigments made from lead or lead ores which annually had ever been produced in the United States. The ordinary formula for white lead is given as $2PbCO_3.Pb(OH)_2$, corresponding to the compositions shown here.

I	per cent
Lead Carbonate	68.91
Lead hydrate	31.09
	100.00

II	per cent
Lead	80.12
Equivalent to	
Lead oxide (PbO)	86.31
Carbonic acid (CO_2)	11.38
Water (H_2O)	2.31
	100.00

The evidence that there is a definite compound of this composition is found in the following facts:

First. If carbonic acid gas is passed into a solution of basic acetate of lead, a precipitate is obtained which, at first, may contain a large percentage of basic acetate of lead in more or less insoluble form. As the solution becomes more nearly neutral, however, the composition of the precipitate approaches that given above. The basic acetate of lead which has been precipitated with the white lead is dissolved in the more nearly neutral acetate solution. The indications are that the chemical process in the corrosion of white lead by the Dutch process, involves, at the start, the oxidation of the lead and the formation of basic acetate of lead; that this basic acetate of lead is decomposed by the carbonic acid present, the basic lead being precipitated as white lead; and that the

neutral acetate of lead again acting upon more metallic lead is changed into the basic form ready to be acted upon again by carbonic acid. The precipitation of white lead, therefore, from solutions of basic acetate of lead corresponds to the formation of white lead in the stacks after the metallic lead had become oxidized.

Second. Any one who is familiar with the Dutch process of corrosion can, on visiting the corroding stacks, isolate definitely, to his own satisfaction, white lead of theoretical composition. His examination of white lead in the stacks is similar to the examination of the mineralogist who selects pure crystals, which he analyzes and finds to have definite composition. Other formulæ for white lead have been suggested, but apparently only by those who have analyzed commercial samples and who have not been familiar with the process itself. It is true that commercial white leads may contain a higher percentage of carbonate of lead than that shown by the theoretical formula; this is due to the fact that the corroding operation is not under complete control. At times, carbon dioxide will be in excess, and it will then, in the conditions in which the white lead exists, act upon the white lead, converting it to neutral carbonate.

There is no evidence that a limited excess of carbonate of lead in white lead is objectionable. Some advocate a percentage higher than the theoretical. It would appear proper, however, that some reasonable limit should be placed upon this excess. What this limit should be can be determined only by thorough physical and practical tests.

It is apparent then, that white lead cannot be considered as a mechanical mixture of carbonate and hydrate of lead. It is possible that hydrate of lead can be mixed with carbonate of lead, and be made to combine, but there is no evidence that the properties of white lead are the properties of carbonate of lead and hydrate of lead separately considered.

The question has arisen as to the proper chemical name for white lead. It may be questioned as to whether it is desirable in all or many cases to use chemical names for commercial products. Commercial products are seldom approximately composed of a single pure chemical constituent, and by using a chemical name for a commercial product we presuppose approximate purity. Chemists, of course, in making their analysis, obtain chemically pure precipitates, but, in the case of mechanical mixtures, the results obtained by analysis are of value in proportion as they are expressed in percentages of the original proximate constituents and, in so far as possible, in commercial terms.

Now especially is this true in the case of white lead, for in the writer's opinion, there is no thoroughly satisfactory chemical name current for even pure white lead. The most common name is "basic lead carbonate"

but this is not satisfactory in that it is not sufficiently descriptive. It is possible to have anhydrous basic compounds. The name "hydrated basic lead carbonate" is equally unsatisfactory, for the reason that the word "hydrated" may refer to water of crystallization, as in the case of so-called "fully hydrated calcium sulphate." Probably, the best name for chemically pure white lead is "lead mono-hydrate dicarbonate," which is exceedingly cumbersome and not likely to be substituted for the simple name white lead, which will probably continue to be used as answering all practical purposes.

Lead. Lead is usually found as an ore in combination with sulphur as lead sulphide or galena. Galena is usually associated with other

Fig. 174.—Casting Lead "Buckles."

minerals, from which it must be separated. This is done by crushing, grinding, and concentration until rich "concentrates" are obtained.

The "concentrates" are roasted and smelted. By this treatment the sulphur is driven off and crude lead obtained. This crude lead is then refined to remove the copper, silver, and other impurities, and "corroding pig lead" is obtained.

For the manufacture of white lead a very pure pig lead is needed, especially in such processes as do not result in the removal of some of the impurities during the manufacturing operation at some point.

There is probably no other chemical product for which more patents have been taken out claiming to revolutionize processes of manufacture. Some of these have been tried on a commercial scale and some have not passed beyond the issuance of patents. Most have been ineffective.

To-day in the United States there are four processes in practical commercial operation. These are the Dutch, the Carter, the Matheson and the Rowley or Mild Process. All of these processes except the Mild Process use acetate of lead as an assisting agent in the process. The great bulk of white lead in the United States is manufactured by the Dutch Process. Next in volume of product is the Carter Process.

The Dutch Process

Corroding. To change pig lead into white lead, it is subjected to the corroding gases produced by the fermentation of refuse tan bark. Special buildings are provided for this purpose, known as "corroding

Fig. 175.—Setting Lead "Buckles" in Pots.

houses." These "corroding houses" are buildings about 30 ft. high with floor-space usually about 20 ft.×40 ft. The floor of this building may be of ordinary earth, and upon it a layer of spent tan bark is placed about 20 ins. thick. On this is placed a layer of corroding pots covering the entire floor, except around the edges where tan bark, known as "banking," is packed.

In each corroding pot a half pint of weak acetic acid, containing about 28 per cent of glacial acetic acid, is placed. These pots are then filled with lead buckles. On top of the pots is placed a layer of boards, and on these boards another layer of tan bark. Another layer of pots is placed on this second layer of tan bark; these pots are filled, as with the first layer, and other layers are placed on this until there are from 8 to 10 layers or "tiers" in the stack.

For the corrosion of lead to white lead, a certain amount of ventilation is necessary so that the moisture can be carried off from the stack. This is done in various ways. A typical way is to provide a wooden pipe that shall run from each tier up near the center of the stack to the top. On the top of this pipe is an outlet which may be opened or closed as may be desired.

Chemical Change. When the stack has been built, the tan bark commences to ferment, liberating carbon dioxide, and generating considerable heat. The heat causes the acetic acid to evaporate and its fumes attack the lead buckles. In a short time these buckles are covered with a layer of

Fig. 176.—Starting to Strip Stack.

basic acetate of lead. The carbon dioxide generated by the fermentation of the tan bark decomposes the basic acetate of lead, producing white lead or basic carbonate and liberating neutral acetate of lead which has a strong solvent action upon lead itself. This fermentation and corrosion of the lead continues until most of the lead is changed into white lead. At times, the heat generated by the fermentation of the tan bark rises rather high, often exceeding 180° F.

Grinding. When the fermentation of the tan bark has practically ceased and the corroding action is nearly finished, the "stack," as the whole body of tiers is called, is taken down, or "stripped," commencing at the top. The corroding operation takes from 100 to 130 days. When the stack is stripped, it is found that the metallic lead originally in the pots has been changed to a white, porcelain-like material, known as white lead. Usually all of the metallic lead originally present has not been corroded. It is necessary, therefore, to remove the unaffected lead before grinding for paint material. This work is done largely in iron machinery that is air-tight, so that the dust formed will not escape. The

corroded lead from the stacks is first passed through a screen, covered with sheet-steel perforated with rather large holes. This screen tumbles the lead about, breaking up the white lead sufficiently, so that it passes through the holes in the steel covering, while the large pieces of metallic lead pass out as tailings, to be re-melted for further use. The coarse white lead is passed through rolls and fine screens to remove the finer metallic lead; following which, the white lead reaches the condition known as "unground carbonate" and becomes suitable for water-grinding. The unground carbonate is mixed with water and ground between high-speed millstones to such a fineness that every particle will eventually pass through fine silk bolting cloth. The white lead suspended in water

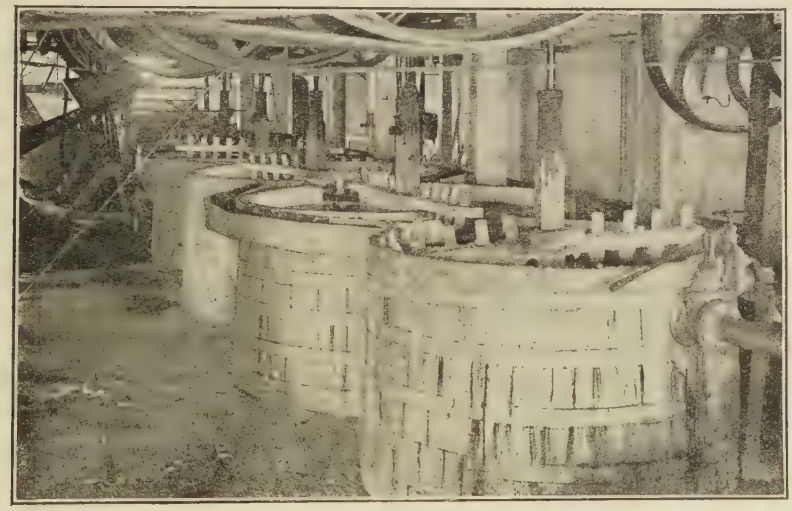

Fig. 177.—Rake Tubs, through which White Lead is Floated.

is floated a long distance so that any coarse and underground particles may settle out. The water containing the white lead is pumped into large tanks and allowed to settle.

Pulp Lead. The thick mixture of white lead and water, called "pulp," which settles to the bottom, is pumped onto drying pans made of copper and dried with exhaust steam, the product being the dry white lead of commerce. This dry white lead is mixed with linseed oil and ground through buhr mills to produce a white lead paste, which is the commercial white lead in oil. Sometimes the white lead pulp is mixed directly with refined linseed oil in special mixers; the oil thus combines mechanically with the white lead, producing white lead in oil, water being eliminated. Certain points in connection with the manufacture of white lead by the Dutch process deserve special consideration.

Corroding Pig Lead. In the Dutch process a very pure pig lead is needed, as the more objectionable impurities are not eliminated to an

appreciable extent in the process of manufacture. There are few, if any, metals found in commerce as pure as the best grades of corroding lead. Silver and copper are, however, the most objectionable impurities, and neither should exceed 0.0010 per cent. In zinc desilverization by the Parkes process, both silver and copper are removed well below this limit. Bismuth is a common impurity in pig lead; it is not removed by the Parkes process. Refining by the electrolytic process, or by crystallization, as in the Pattison process, eliminates bismuth. Bismuth is objectionable as it imparts a gray tone to white lead containing it. The manufacturing difficulty occasioned by bismuth is to be found in its tendency to collect on the millstones in an alloy of lead and bismuth somewhat richer than the original pig lead. Iron does not alloy with lead appreciably, so that in melting pig lead to cast it into buckles, the iron, which may have been present in the pig lead as a mechanical impurity, is eliminated. The maximum solubility of iron in lead is about 0.0015 per cent.

While a very pure pig lead is needed for the manufacture of white lead by the Dutch process, this does not necessarily operate against the process as an element of cost, as the refining of lead is a desilverizing process, and the silver recovered generally pays for the cost of refining. Attempts to manufacture white lead from the low grades of pig lead running relatively high in silver and copper should not, consequently, be favored from the standpoint of economy of operation.

Acetic Acid. The amount of 28 per cent acetic acid lost in the corrosion of white lead by the Dutch process seldom exceeds 1 per cent of the lead set. Some of this acetic acid is carried away in the flue gases, some is eliminated in the wash-water, and the remainder stays with the white lead, combined in some form of insoluble acetate. Ordinarily the amount of acetic acid present is about 0.08 per cent. There is no evidence, based on practical experience, that this acetic acid is objectionable. There is strong evidence that a very much larger percentage of acetic acid may be present without appreciable injury to the product. Very carefully conducted painting tests show no difference in durability between the ordinary Dutch process white lead and one to which acetate of lead, equivalent to 0.50 per cent of glacial acid has been added.

Fermentation. The micro-organisms, which are in part the cause of the generation of carbon dioxide from the tan bark, have not been isolated, and, so far as is known, attempts that have been made have been unsuccessful in obtaining pure cultures. The indications are that the oxidation of the tan bark in the early stages of the corroding action is due to fermentation produced by micro-organisms, but, when the heat has reached a certain point, the oxidation is in the nature of slow combustion, in which micro-organisms have little or no part.

Pulp-mixed White Lead. It has been mentioned that white lead in water can be mixed with linseed oil, with the result that the oil displaces

the water and combines mechanically with the white lead. This is the basis of pulp-mixed white lead. Its manufacture is more sanitary than dry grinding, and is the principal reason why the pulp-mixed process has become popular. Pulp-mixed white lead, also, is somewhat whiter than dry ground, because there is less overheating in the mills, while some of the mechanical impurities, such as tan bark, are eliminated with the water. The amount of water left in pulp-mixed lead seldom exceeds 0.50 per cent, and usually is much less. There is no evidence that this water operates injuriously upon the paint prepared from pulp-mixed lead, nor is there any evidence that pulp-mixed lead is inferior in any respect to the old-fashioned lead ground in chasers and then through buhr mills. Evidence, on the other hand, has been obtained that pulp-mixed lead is equal in all its qualities to dry ground, and, in addition to that, it works somewhat better for inside work where what is known as "flat work" is done.

The Carter Process

Chemically, white lead manufactured by the Carter process is the same as when manufactured by the Old Dutch process. In each case pure metallic lead is converted into basic lead acetates which are acted upon by carbon dioxide to form basic carbonate of lead, or white lead.

The Carter process starts with pig lead, a grade commercially known as "corroding," which is as free as possible from bismuth, antimony and other impurities.

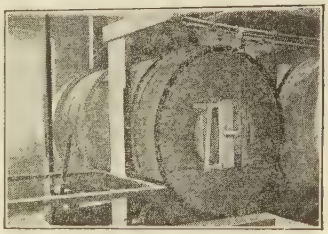

Fig. 178.

The first step is to atomize the metallic lead, the method being substantially the same as atomizing a liquid in the ordinary nasal atomizer. The pig lead is melted in a kettle to which is affixed a nozzle through which the molten lead flows by gravity. At the outlet it is struck by a jet of superheated steam which atomizes or blows the lead into very fine particles which are very slightly oxidized.

In some text-books on paints and paint pigments, the Carter process is referred to as "the quick process." This is a little misleading, for while the time of corrosion is cut down from about 120 days by the Dutch process to about fifteen days, the mass of metallic lead exposed to the corroding agencies is reduced in much greater proportion.

The powdered lead, in charges of about 4000 pounds, is then placed in wooden cylinders about 6 feet in diameter and 10 feet long, which revolve very slowly on their own horizontal axes. The metallic lead in the cylinders is treated with dilute acetic acid and carbon dioxide. A

very weak solution of the acetic acid is sprayed into the cylinders at intervals. The carbon dioxide is admitted through the center of the head and is produced by the perfect combustion, in the presence of an excess of oxygen, of carefully selected coke. The coke is burned under boilers so as to utilize its caloric value. The lead in the cylinders is kept moist with water during corrosion and a certain per cent of oxygen (air) pass into the cylinders with the carbon dioxide.

The action of the acetic acid upon an excess of metallic lead and lead oxide produces various basic lead acetates. The carbon dioxide acting on the basic acetates forms basic lead carbonate or white lead. The acetic acid, freed by the action of the carbon dioxide on the basic acetates, acts again on the excess of metallic lead and lead oxide and is again liberated, and so on in cycles until corrosion is complete.

As the cylinders, Fig. 178, slowly revolve, the pulverized lead is carried upward on the interior of the cylinder and rolls down to the bottom, exposing new particles to the corroding agencies. The heavy mass also performs most efficiently the functions of a tube mill in grinding the carbonate off the metallic particles as fast as it is formed and reducing it to an exceedingly fine powder.

By the Carter process corrosion is complete in about fifteen days. No artificial heat is required, sufficient heat being generated by the chemical combination to keep the contents of the cylinder at about 145° F. during corrosion.

At the proper stage, the cylinders are emptied and the white lead is then washed and agitated in water, removing any traces of acetic acid or acetate of lead. It is then floated in water to remove the small particles of coarse lead, if any, and is then pumped into storage tubs, where the lead settles in the form of a heavy pulp. After evaporating the water from the pulp, the result is commercial dry white lead.

For general use, white lead is put up in stiff paste form to facilitate mixing into paint. This paste consists of 92 per cent of hydrated carbonate of lead and 8 per cent of pure raw linseed oil. This paste is produced in two ways: one by chasing, mixing and grinding in a double set of heavy buhr-stone mills, dry white lead and pure linseed oil; the other by mixing the lead pulp (lead and water) with linseed oil in what is known as pulp machines, the white lead taking up the oil to the exclusion of the water and becoming "lead in oil" which is then chased and mixed and run through the heavy buhr-stone mills. The pulp process simply does away with drying the lead pulp, and the only purpose of the heavy grinding is to secure complete incorporation of the lead and the oil. Properly ground lead in oil, ground either dry or from pulp, does not contain more than 0.5 per cent of free moisture.

The last step in the Carter process is to convey the paste white lead from the mills to storage tanks, each of 75 tons capacity, where it is allowed to stand for several days before it is drawn off and filled into

kegs. The pressure of the lead in these tanks completes a perfect saturation of the lead with the oil and forms a very smooth, unctuous paste.

The Matheson Process

This process is a development of the process usually attached to the name of Thenard, who introduced it at Clichy, France. It involves the use of a solution of basic acetate of lead into which carbon dioxide more or less purified is conducted. The carbon dioxide combines with the basic lead removing it from its combination as acetate of lead, the carbonate compound separating as a precipitate of white lead. The white lead thus produced is removed by filtration, washed with water and dried. The nearly neutral lead acetate is then recharged with lead oxide to bring it to the proper basicity and the operation repeated. The lead acetate acts therefore as a carrier for the lead and theoretically should all be recovered. A small amount of the acetate of lead remains with the white lead however, probably as a hexbasic acetate.

The Rowley or Mild Process

This process although similar to, differs from, the Carter Process in that no acetic acid is used. It had long been assumed that white lead could not be made without a carrier like acetate of lead. The advent of this process shows that this assumption was erroneous. The lead is atomized in a manner similar to that used in the Carter Process. The atomized lead after proper floatation is run into oxidizers which consist of mechanically agitated tanks containing water into which air under low pressure is forced. The oxide of lead so produced—which may be more or less in the form of hydroxide is floated away from the unoxidized metal and run into carbonators which are horizontal rotating cylinders where under the action of carbonic acid gas (contained in purified flue gas) white lead is produced. It is then allowed to settle and the thickened pulp is pumped onto drying pans and dried.

The Euston Process *

"The Euston process for the manufacture of white lead has been developed to commercial success during the past seven years, and is now owned and used by Euston Process Company, of Scranton, Pa., which has recently enlarged its plant to a capacity of 8000 tons per annum. The principle underlying this process is that white lead, contrary to the usual view that it is a single compound is a mixture of a basic carbonate of lead of the approximate composition $PbCO_3 \cdot Pb(OH)_2$, in variable proportions with substantially normal lead carbonate, $PbCO_3$; and that, by

* Private communication from Edwin Euston.

the separate preparation of these two components and their later admixture in equivalent portions, white lead analyzing $2PbCO_3 \cdot Pb(OH)_2$ is obtained. By varying the relative quantities of the two components, the composition of the white lead can be varied at will.

"The process uses the Thenard method of precipitation from basic lead acetate solution by carbon dioxide gas, but with the distinctive patented features that (1) to produce a basic carbonate, $PbCO_3 \cdot Pb(OH)_2$, the treatment with carbon dioxide gas is stopped before the solution becomes acid in reaction; (2) to produce a substantially normal carbonate $PbCO_3$, the treatment with carbon dioxide gas is continued until the solution becomes acid in reaction; and (3) to form white lead the separately formed basic carbonate and the substantially normal carbonate are mixed. The process is readily controlled at all stages by means of sensitive tests devised, and uniformity of product is therefore obtained. The type of apparatus used is distinctly original, and is of importance in governing the physical characteristics of the white lead produced.

"The process retains the hygienic feature of the Thenard method, and is the only precipitation process yet devised which meets successfully the commercial specifications and requirements in the white lead produced. The characteristics of the product are greater uniformity, fineness, whiteness and freedom from metallic and "sandy" lead. Ground in 10 per cent linseed oil to a moderately stiff paste, it requires for reduction to painting consistency only the same amount of oil as white lead made by the stack process, and is equal in opacity."

The Value of White Lead as a Pigment. That white lead is the only white pigment which has been generally and successfully used, at least in this country, as a pigment by itself is a fact which requires no demonstration. Some of the reasons that have been assigned for this superiority of white lead are untenable. The commonest explanation advanced for the superiority of white lead is that it enters into combination with linseed oil, forming a lead soap. It has been said that the hydrate of lead combining with the linseed oil in this way gives to white lead paint its working qualities and, as a supplement of this theory, it has been asserted that it is the carbonate of lead that gives to white lead its body. So many eminent authorities have accepted and advocated this theory that we feel some hesitancy in questioning it. It would appear, however, that there is little ground for the belief that white lead combines with linseed oil, except to an almost inappreciable extent. Hanney pointed this out many years ago when he found that by the extraction of white lead paste he was able to obtain practically all of the linseed oil it contained in its original form. Hanney's work has been duplicated by the writer on many occasions, confirming his results and conclusions.

It is true that white lead can be made to react on linseed oil at about the temperature of boiling water, but even then the reaction is

only slight, unless the heating is prolonged for some time. White lead contains about 31 per cent of lead hydrate. Figuring from the saponification value of linseed oil, which we place at 190. 100 lbs. of white lead would require 76 lbs. of linseed oil to combine with this lead hydrate. It is seen, therefore, that, in a white lead paste containing 10 per cent of linseed oil, there is a large excess of base which would insure the complete saponification of the oil if such a reaction should take place.

On extracting white lead paste with ether, it is found that the linseed oil obtained contains a very small percentage of lead. The lead soaps obtained by precipitating the fatty acids of linseed oil with a lead compound dissolve readily in ether, with the exception of the lead soaps of the saturated fatty acids, so that practically all lead compounds would be dissolved by the ether. White lead adds to the drying qualities of linseed oil with which it is ground to the extent of this very small amount of lead, which combines with the linseed oil and dissolves in it.

As linseed oil paste does not show a combination of the white lead with the linseed oil, so it is also found that where an excess of oil is used there is no appreciably amount of combination between the hydrate of lead present and the linseed oil. Whether there is any combination between oxidized linseed oil and white lead after a paint has been applied is not definitely known. We have, however, no evidence that such a combination takes place, and it seems improbable that it does.

The conclusion, then, is that white lead is a relatively inert pigment, entering into combination to only a slight degree, if at all, with linseed oil or any of its constituents, when mixed with it as a paint.

Lead Poisoning and its Prevention. In operations involving the use of lead or its compounds there has been in the past considerable suffering from lead poisoning. A study of lead poisoning and the methods which can be adopted for its prevention indicate that with proper sanitary provisions lead poisoning can be reduced to a negligible amount. This has been the experience in Europe and the United States.

To bring this desired result about, it has been necessary to develop a sentiment in favor of the proper control of manufacturing operations involving the use of lead, together with a proper recognition by employees of the dangers to which they are subjected and the responsibilities which rest upon them to co-operate with manufacturers in the avoidance of those dangers. It is perfectly obvious that the whole progress of civilization consists in the intelligent control of dangerous things. Fire is a very destructive force, but properly controlled it has given us our steam engine and power-producing plants. Electricity has killed a great many people, but by a proper knowledge of insulating materials and the dangers connected with the handling of electrical apparatus, injury and death from the

electric current in industrial operations has been rendered infrequent. By the proper harnessing of our water supplies, they have changed from a destructive force into engines of huge service. In every industry there are hazards peculiar to that industry, which intelligent study leading to proper control can eliminate. In this respect the lead industries are in no way peculiar, as the following account will show. If manufacturers install the proper sanitary equipment and if employees follow simple sanitary practices lead poisoning is avoided.

The following statement with regard to lead poisoning from the physician's standpoint has been prepared by Dr. George E. Brockway, attendant physician at one of the branches of the National Lead Company.

Plumbism. "Plumbism or lead poisoning has been known for several centuries. We know that Hippocrates recognized it and that Raphael and Michael Angelo acquired it through mixing their own paints. However, it was not accurately described until 1839, when Tanguerel des Planches published a symposium on that subject.

"Lead in any form may be poisonous, but the fumes from molten lead and dust from the finer crystal salts or compounds are responsible for the greater number of saturnine intoxications.

Occurrence. "There is a belief that a great difference in individual susceptibility to the toxic action of this metal exists, and one can not tell whether the strong and robust or the weak and sickly will become a victim. Of course generally speaking, those in good health will withstand the greater exposure, but not infrequently one finds a healthy subject is poisoned by the minutest quantity, whereas a thin, anæmic workman may show no symptoms after years of exposure in most unsanitary surroundings.

Pathology. "The pathology is rather obscure for the lesions caused by lead are mostly not typical as they are also found in many other diseases and conditions. The one typical lesion is a stippled, bluish-gray line found on the portions of the gums contiguous to the teeth. This is due to a deposit within the substance of the gums, and as it cannot be brushed off it is easily differentiated from the so-called dust line found in any dusty trade. The granular degenerations appearing in stained smears as little black dots within the red blood cells are perhaps the next most typical lesion, though these may be seen in any case of severe anæmia.

"The other pathological conditions caused by lead are catarrh of the stomach, chronic gastritis, acute and more often chronic kidney trouble. In cases of long duration hardening of the arteries and subsequently enlargement of the heart along with degeneration of its muscle fibers occur. Inflammation of the nerves of the hands and sometimes of the feet may arise and manifests itself at first as tingling, burning, weakness or numbness, and later if untreated there is a paralysis or atrophy of the

extensor muscles of these members, resulting in wrist or foot drop. Lead pigment in severe cases may be isolated from stomach, liver, kidneys, blood, lungs and brain, showing that this insidious poison permits neither alimentary, excretory nor nervous systems of the body to escape its ravages.

Symptomatology. "The common classification of the symptoms due to lead are usually grouped under the two heads of absorption and intoxication. Lead absorption means slight poisoning, just as surely as lead intoxication means greater poisoning, so it is better not to confuse ourselves with these useless terms.

"The most common primary symptom due to lead is stomach or intestinal distress which manifests itself as a burning sensation, slight pain, nausea, constipation or feeling of fullness. These symptoms grow more intense until there is constant nausea, vomiting or acute cramping abdominal pain, together with slight or intractable constipation. Oftentimes the occurrence of a slight tendency to constipation in an individual, who has previously been free from such a condition, will clinch the diagnosis of lead poison. Headaches of a chronic character, dizziness and disturbance of vision are not infrequent occurrences in lead workers.

"The danger line symptoms are almost always preceded by pain and there are few diseases that may cause so many different types of pain. The workers who inhale dust of the molten metal are prone to develop nerve, bone and muscle pains, seemingly being more or less immune to the gastric intestinal symptoms. Backache, most often in the lower lumbar region, is complained of by fully two-thirds of the cases which I have seen, and vague muscle and joint pains are experienced by the other third. The shoulder joints and wrists are more often affected than the other joints of the body. Bone pains, especially along the shin bones, may be very persistent, transforming the nights into hours of constant suffering. Like other diseases, the symptoms of lead poisoning are most troublesome at night. Perhaps the afflicted is distracted during the day and does not notice his suffering, or the fatigue of his day's work may make the nerves more susceptible to the action of the poison.

"The brain and central nervous system do not escape the action of lead, and in cases of a chronic character severe headache may be very persistent. Lead psychosis, acute or chronic, is now a rather rare condition which used to be very common before modern methods of sanitation became effective. The acute form is preceded by several days of severe headache and is soon followed by active delirium, gradually changing to a stuporous sleep, and very often terminating in convulsions and death. The chronic form simulates the psychosis of dementia paralytica (insanity with paralysis) and is not infrequently confounded with it. Recovery from the acute form occasionally occurs, but is very rare in the chronic type.

"The toxic action of lead does not cease with the sufferers themselves but may be passed on to their offspring. Prematurity, idiocy and infantilism have often been observed among the families of those suffering from lead poisoning.

Lead as a Factor in Other Diseases. "All the dusty and gaseous trades predispose to pulmonary disease and lead is no exception. This can be easily explained because any irritating substance inhaled makes the pulmonary tissues susceptible to infection. Any lead worker who suffers from anæmia, has an impoverished condition of the blood, which presents a sorry barrier to any infectious disease.

Prevention. "Proper sanitation in the lead industries will prevent the major portion of the poisonings from this cause. The factories should have free circulation of fresh air with proper suction ventilators, dustless walls and floors, or at least adequate measures to prevent the dust from flying about. All melting pots, furnaces, grinders and dusty machinery should be protected by suction hoods and the products of these machines should be mechanically emptied into covered conveyers. Workmen should have clean overalls, respirators and adequate facilities for bathing of the entire body. No food should be consumed before washing the hands and face and then only in rooms provided for that purpose. Separate lockers should be provided for working and street clothing and the men should be encouraged to keep their working clothes clean or supplied frequently with clean overalls. Weekly or at least monthly medical inspection of the workers will usually prevent any serious poisonings by weeding out the susceptibles and afflicted and advising the well how to continue healthy.

"After all these safeguards have been provided it is absolutely imperative that they should be frequently inspected and that the workers should be compelled to observe the rules of the factory.

Treatment. "The treatment of lead poisoning should be supervised by a physician and the indiscriminate use of cathartics, sulphuric acid lemonades, aspirin and other patent pain relievers, can only do ultimate harm. The drugs that are supposed to eliminate lead are few and of doubtful value. Constipation should be combated by vegetables, fruits and bran foods with the aid of plenty of water and mineral oil. Neuritic patients need mechanical devices for the prevention of deformities and properly graded massage and electric treatment after the acute symptoms have subsided. Fresh air, plenty of fresh food, abstinence from alcohol and daily bowel movements are more important than all the drugs which the physician has in his armamentarium."

According to the best information obtainable to-day lead as a poison enters the system only through two channels, the mouth and the nose. There is a difference of opinion as to whether lead is absorbed more in the lungs or in the digestive tract. It has been fairly well established, however, that if lead does not enter the mouth or nose, workmen are practically

free from danger of poisoning. With this simple proposition in mind the following practical conclusions may be drawn:

To avoid lead poisoning, no food should be eaten where manufacturing operations, expecially those of a dusty character, are carried on, nor should water nor other liquids be drunk in such places. The hands and faces of workmen should be scrupulously cleaned before eating. To facilitate this cleaning workmen should not have whiskers or mustaches, especially the latter, which are apt to prevent the proper removal of lead dust. In especially dusty places respirators should be used.

In order to make the surroundings of workmen in the lead industries more sanitary suitable apparatus should be installed to prevent dust from getting into the air and to remove it immediately if this is not practicable. As far as possible lead products, etc., should be handled by machinery and not by hand. Several States, following the lead and advice of the American Association for Labor Legislation, have adopted restrictions and regulations regarding the manufacture of lead products. In the main these laws have appeared satisfactory, probably because most manufacturers have been glad to co-operate voluntarily in carrying out their provisions.

It has been difficult, however, to reach certain classes of users of lead products, particularly house painters. There is little danger in exterior painting on account of the dust which may arise from sandpapering, although there is still danger of lead poisoning through lack of cleanliness on the part of workmen; but on interior painting there is considerable danger of lead poisoning if dry sandpapering processes are followed. It has been found, however, that by the use of mineral oils having a safe flash point, sandpapering can be done without much dust being formed the paper being dropped into the oil before using. An oil of this kind should be completely volatile and have a flash point above 100° F. Kerosene oil or coal oil may be used, but if it is used the part sandpapered should be cleaned with benzine or a similar light solvent.

One of the most important things about a lead factory is to keep things clean. It is very desirable to have floors that can be flushed down with water or at least swept up very frequently with wet sawdust. All machinery as already indicated should be dust tight. When lead products can be handled in the wet state manufacturing operations are more healthful. The repairing of machinery is most dangerous as the machines have to be opened and subject to more or less shock, which loosens the dust. Under such conditions respirators or other protective measures should always be adopted.

Lead poisoning occurs in some kinds of lead mining, particularly in the case of what are known as the dry or oxidized ores. It has been stated, however, that in the mining of sulphide ores lead poisoning seldom occurs. In lead smelting until recent years, lead poisoning was quite prevalent, but it has been largely avoided by the use of suitable dust and fume

collecting devices and the doing by mechanical means of what was theretofore done by hand. In the handling of metallic lead in the solid state very little dust is formed and very little poisoning occurs. When lead is melted, however, it tends to dross, and if agitated this dross may be carried into the air. In order to prevent lead poisoning from such dust suitable ventilating appliances should be used. Lead itself is less volatile than its oxides, but all of these volatilize at so high a temperature that it seems improbable that lead in the gaseous or true vapor form is ever the occasion of lead poisoning.

Type setters have been subject to lead poisoning very often due to the dust formed by the attrition of type. With modern type-setting

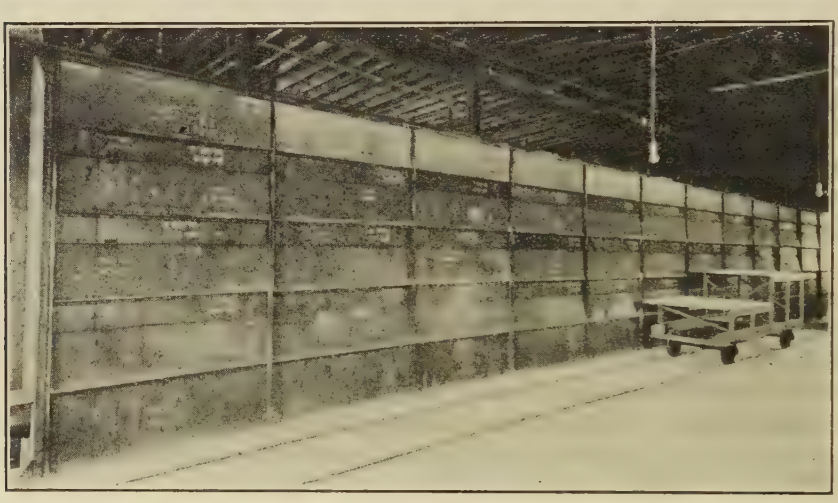

Fig. 179.

machines, however, this is largely avoided. Where the old hand type-setting exists vacuum systems of cleaning the trays should be used.

In the manufacturing of white lead by the Dutch process lead poisoning may occur in the stacks from the dust that may arise from the lead in the tan bark or the dust that may arise in emptying corroding pots. Modern methods of preventing this dust from rising from the white lead have been devised and by keeping the tan bark moist comparatively little dust rises from that source. In all modern white lead plants where the white lead is dumped into and received by the mill, strong fans are in operation to draw all dust away from the workmen. From this time on the white lead is passed through iron-clad, dust-tight machinery until it is wet with water, after which there is little danger except in the drying of white lead. The danger from this latter source, however, has been avoided by enclosing the drying pans (see Fig. 179) and drawing the white lead into a space between the pans to the outer enclosure, at the bottom of which a conveyor runs. Under these conditions the

workman is not subjected to dust arising from the white lead on the drying pans.

In the packing of dry white lead there is danger of lead poisoning unless a proper exhaust is provided around the packing machines. In the manufacture of oxides of lead, lead poisoning may arise through the handling of the dry oxides, but this can be largely avoided by having the furnaces discharge directly into conveyors with proper ventilating appliances and proper hoppers to receive the furnace products. From that time on the danger is limited to the packing of the oxides and to such repair work as may be needed from time to time. In the manufacture

FIG. 180.

of salts of lead such as acetate of lead, etc., very little dust is occasioned, and if the workmen keep themselves reasonably clean little danger of lead poisoning should exist.

To prevent lead poisoning as an occupational disease the best opinions seem to indicate that the following requirements are reasonable and just:[1]

Every employer should do all that can be reasonably expected of him to prevent lead poisoning. Work rooms should be well lighted and ventilated. Rooms in which the work is of a dusty character shall be separated by partition walls from all other work rooms. All floors shall be of a kind that will permit of the easy removal of dust by wet methods or vacuum cleaning; such floors shall be cleaned daily. All kettles, etc., in which the lead is being melted shall be provided with hoods con-

[1] These requirements are abstracted from the Standard Bill of the American Association for Labor Legislation and the Pennsylvania Code now under consideration.

nected with an efficient air exhaust. All receptacles in which lead compounds in the dry form are being conveyed from place to place shall be fully equipped with an efficient air exhaust at the place where they are being filled or discharged. All machinery handling lead products shall be effectively closed and connected with an effective air exhaust.

The collection of the dust from such places as require an air exhaust shall be accomplished by a cloth dust collector having an area of not less than one-half of a square foot of cloth to every cubic foot of air passing through it per minute, the dust collector being placed in a separate room

Fig. 181.

to which no employee shall have access while the works are in operation except for essential repairs. Other equally efficient dust collecting devices may be used.

All employers shall provide wash rooms (see Fig. 180) entirely distinct from work rooms and equipped with proper washing facilities. Where basins are provided there shall be at least one basin for every five such employees, and when troughs are provided at least 2 ft. of trough length for every five employees. Employers shall provide nail brushes and soap and at least three clean towels per week for each such employee. A time allowance of not less than ten minutes at the employer's expense shall be made to each such employee for the use of said wash room before the lunch hour and at the close of the day. One shower bath shall be provided for every

five employees. The baths shall be approached by wooden runways with movable floor gratings and be supplied with controlled hot and cold water. Time allowance shall be given of ten minutes at the employer's expense to each employee for the use of these shower baths at least twice a week at the close of the day's work. Employers shall keep a record of the use of these baths by each employee.

Dressing rooms separate from work rooms shall be furnished with double sanitary lockers, one for work clothes and the other for street clothes. Eating rooms shall be provided separate from work rooms (see Fig. 181). No employee shall be allowed to take any food or drink into any work room or be allowed to remain in the work room during the time allowed for his meals. Sanitary drinking fountains shall be provided.

Employers shall provide at least two pairs of overalls and two jumpers for each employee, repairing and renewing them when necessary and washing them weekly. Such clothing shall be kept exclusively for the use of that employee. At least two effective respirators shall be provided and renewed when necessary for each employee who is engaged in any place where lead dust is produced. Employees are required to make use of all these facilities and proper notices shall be placed around the factory in languages legible to all employees calling attention to the dangers of lead poisoning and specifying the above requirements. The contents of these notices shall be explained from time to time to those employees so that there can be no doubt of employees having their attention called to them.

Licensed physicians designated and paid by the employer shall examine workers in the manufacture of lead products at least once a week and reports of these examinations shall be available for the use of state authorities. If any employee should on the examination of the physician be found to be affected by lead poisoning the employer shall discontinue the use of said employee in any departments exposed to lead dust until a written permit has been furnished by a licensed physician. No female of any age shall be permitted to handle dry lead compounds. No male employee less than twenty-one years of age shall be permitted to engage in any processes involving the production of lead dust. The employment of any-one using alcoholic liquors should be avoided. The chewing of tobacco should be avoided in the presence of lead dust.

Since and wherever the above regulations have been fully complied with serious lead poisoning has become practically eliminated.

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CHAPTER XIV

ZINC OXIDE

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Historical. Though this material was known as a laboratory product in the eighteenth century and was, from time to time, mentioned and offered as a possible substitute for white lead, it was not until towards the middle of the nineteenth century that it became commercially available as a painting material. Its production on a practical scale was due to the labors of Le Claire, a contracting painter and philanthropist of Paris, and his friend, Sorel, an industrial chemist, to whom also is due the invention of "galvanized" iron. Le Claire's motives were philanthropic. His desire was to produce a satisfactory white pigment to replace white lead and thus to eliminate the danger of lead poisoning.

Le Claire, being what we should to-day style a "socialist," was especially concerned with the situation as he found it among his own employees. To him is generally accorded the honor of introducing Zinc Oxide as a pigment, though his larger fame comes from his repute as "the Father of Profit-Sharing," which system he established not only in his own shops, but also in the Compagnie de la Vièille Montagne, to whom he transferred his process for the manufacture of zinc oxide.

His establishment secured a number of painting contracts from the Government. These he executed with zinc oxide, acknowledging the fact after attention had been called to them by their superior durability and permanence of color.

The ultimate result of the controversy then started was a series of Government restrictions prescribing the substitution of the new pigment for white lead in various departments. These restrictions have lapsed and been revived from time to time, but finally in 1915 a law went into effect prohibiting the manufacture or use of white lead in France.

This law will undoubtedly entail a distinct inconvenience upon the paint consumers of France, since white lead is a valuable and useful pigment, especially in combination with zinc oxide, and its toxic properties are easily avoided by the use of readily enforceable precautions, such as are at present observed by manufacturers in the United States.

It is merely a question of proper protection against dust and of personal cleanliness.

In the Le Claire-Sorel process metallic zinc or spelter is the raw material used. Because it was invented in France it is commonly called the "*French Process*" and the product "*French Zinc*" or "*French Zinc Oxide*"; and because the zinc ores pass through two manufacturing stages, the process is frequently styled the "*Indirect Process.*"

Another process invented shortly after in America by Jones and somewhat modified by Wetherill, produces the oxide directly from zinc ores. From the country of its origin it is known as the "*American Process*" and from its character as the "*Direct Process.*" The products are known as "*American Process Zinc Oxide.*" In this process the character of the ore used determines the nature of the product.

Raw Materials. Any ore of zinc can be used as a raw material for the production of spelter, on the one hand, and thus indirectly for the production of French process oxides, or on the other hand, for the direct production of American process oxides. The ores of zinc, in order of their economic importance, are as follows:

Sphalerite, or "Zinc blende"—zinc sulphide, ZnS, sometimes found practically pure, but generally associated with sulphides of other metals, The approximate composition of pure blende is zinc 67 per cent, sulphur 33 per cent.

Smithsonite, zinc carbonate, $ZnCO_3$. The approximate composition is zinc 52 per cent, carbon 9.6 per cent, oxygen 38.4 per cent; or zinc oxide, 65 per cent, carbon dioxide 35 per cent.

Calamine, hydrous zinc silicate, $2ZnO.SiO_2.H_2O$. When pure it contains zinc oxide 67.5, silica 25, water 7.5.

Willemite, the orthosilicate, Zn_2SiO_4, zinc oxide, 73 per cent, silica, 27 per cent.

Zincite, zinc oxide, ZnO; approximately zinc, 80.30, oxygen, 19.70.

Franklinite, a combination of manganous, ferrous, manganic and ferric oxides with zinc oxide. The formula is $(Fe,Mn,Zn)O.(Fe,Mn)_2O_3$, in which the metallic elements are in variable proportions. The ore from Franklin, New Jersey, averages about the following analysis: Fe 42 per cent, Mn 14 per cent, Zn 16 per cent.

There are various other zinc minerals usually found associated with those above enumerated and utilized with them, but they are, by themselves, of little economic importance.

Preliminary Treatment. The treatment of the ore depends upon its character and its associations. These operations, however, usually involve sorting, crushing, sizing and mechanical separation.

From the point of view of oxide manufacture, the most important ores are those mined at Franklin, New Jersey. This deposit is in many ways unique. Its character and geological significance are discussed at length in Folio No. 161 of the United States Geological Survey. It

consists mainly of Willemite, Franklinite and Zincite in a gangue of calcite; though associated with these are found many other zinc bearing minerals. The ore is delivered on a picking table, where the larger pieces of waste are removed by hand. The residual ore is delivered to rock breakers and thence to crushers, by which it is crushed to buckwheat size. *Franklinite* contains iron oxides and is strongly magnetic. This property is utilized in its separation. The crushed ore is delivered on a belt, by which it is carried beneath the poles of powerful electro-magnets, across which a second belt moves at right angles to the belt carrying the ore. Coming beneath the magnets the Franklinite is lifted to the under side of the transverse belt and by it carried to one side, while the remaining material passes forward to receiving bins. The Franklinite, being carried by the upper belt out of the magnetic field, falls into a separate bin.

When blende is used for the production of oxide it undergoes a preliminary " roasting " by which the sulphur is driven off. As these blends always contain some galenite (lead sulphide) the oxides produced from them or from ores containing them, invariably contain some lead sulphate.

French Process. Spelter or metallic zinc is the raw material. Zinc is a metal whose temperature of reduction is higher than its boiling point. Hence when the temperature is high enough to reduce the oxide of zinc in the ore and liberate the metal, the latter comes off in a state of vapor. This occurs at about 900° C. The production of spelter is, therefore, a process of reduction, distillation and condensation. It is carried out in retorts of special construction, the reduction and volatilization occurring in the retort and the condensation in a fire-clay condenser. Zinc at its reduction temperature combines vigorously with oxygen to form zinc oxide, a fact familiar to all students of chemistry, in connection with blowpipe determinations. On contact with air, zinc vapor promptly takes fire and burns with a characteristic green flame, to zinc oxide, which is yellow when hot and white on cooling.

In the French Process metallic zinc is volatilized in retorts, the issuing vapor is brought into contact with air, and the resultant oxide smoke carried through large chambers, in which it settles and whence it is removed from time to time and packed for shipment.

Le Claire's process differs in some details from Sorel's; but they are the same in principle. The composition of the spelter used, the details of furnacing and the arrangement of the collecting chambers determine the character and grade of product.

French process oxides of American manufacture are known as " Florence Zinc." The best known of the foreign products are the Vielle Montagne oxides, produced by the company originally operating under the Le Claire patents.

French process oxide is sold in three grades, designated respectively as " *White Seal.*" " *Green Seal* " and " *Red Seal.*"

White Seal. This grade is characterized by brilliant whiteness, great volume and extreme fineness. It is packed 150 pounds to the barrel, as compared with 300 pounds of other oxides.

Green Seal. Equal in brilliancy of color to "White Seal" but less voluminous.

Red Seal. The cheapest of the three grades, and neither so brilliantly white nor so impalpably smooth in texture as the others.

American Process. In this process, as already indicated, the raw materials are the ores of zinc. The crushed ore is intimately mixed with fine anthracite and charged in special furnaces upon perforated grate bars. These furnaces are built on the plan of a fire box and are provided with an under-grate blast. The furnace chamber is closed during operation and is opened only during the process of charging. These furnaces are placed back to back in "blocks," and each block discharges the products of combustion and the oxide fume into sheet iron flues which convey them into the collecting system. While charging and discharging, a damper over the furnace is kept closed to prevent contamination of the oxide in the collecting system. The furnace gases are drawn through the flues by a suction fan placed in the line between the furnaces and the collecting system, the fan serving also to deliver the gases and fume into the latter. The oxide together with the gases from the furnace, in their passage to the collecting system are thoroughly cooled, a sufficient length of flue being provided for that purpose.

The collecting system consists of a series of bags suspended vertically from a system of horizontal pipes, which are connected to the flue already referred to. Their mesh is such that it readily permits the escape of the gases, but retains the oxide. From these bags the latter is removed from time to time, properly graded, bolted through silk bolting cloth, and packed by machinery into barrels containing 300 pounds of the oxide.

For the production of leaded zincs by this process, mixed ores are employed; sphalerite and oxidized ores, including both carbonates and silicates. As already stated, sphalerite, when used for oxide manufacture, is treated to a preliminary roasting, which removes the sulphur in the form of the dioxide, the residue being zinc oxide. The method of operation from this point forward is as already described. These ores invariably contain more or less lead, which appears in the product as basic lead sulphate. These leaded oxides are graded according to color and content of lead sulphate. The purest of them contain less than 5 per cent, the most highly "leaded" as much as 30 per cent of that compound.

American Process Zinc Oxides, as produced by the New Jersey Zinc Company, are classified according to physical characteristics, as follows:

Selected. So called because made from selected ore and characterized by superior color, smoothness, and uniformity.

XX. Not quite so uniform in color, nor generally so fine and smooth in texture, as the selected.

Special. Remarkable for its freedom from lead—under 0.1 per cent PbO. Especially intended for use in compounding white rubber. Can be used in any mixture without changing color. Very smooth and free from mechanical impurities.

The American Zinc, Lead and Smelting Co. also produces a lead free American process zinc oxide which is designated as American AAA.

Chemistry Involved in the Process. The chemistry involved in the conversion of zinc vapor into its oxide is, theoretically, very simple, the reaction being expressed by the formula $Zn+O=ZnO$. That involved in the production of the metallic vapor from its ore is more complex. When the ore is a " blende " (zinc sulphide) the first product of oxidation is sulphurous anhydride, SO_2, the residual product being zinc oxide ZnO, according to the formula, $ZnS+3O=ZnO+SO_2$. In some cases the sulphur dioxide is allowed to escape into the air; in others it is further oxidized to SO_3, the production of sulphuric acid thus becoming a subsidiary branch of the industry. With this ore, then, the process of manufacturing the oxide really starts with zinc oxide as the raw material. It will be seen, in considering the remaining ores, that this is always the case.

When carbonate ores (*Smithsonite*) are utilized, carbon dioxide is driven off and goes forward with the furnace gases, leaving zinc oxide as a residue, according to the simple equation $ZnCO_3=ZnO+CO_2$. Here again we have zinc oxide as the real raw material in the oxide furnace.

With the silicates the silica takes no part in the reaction, remaining behind as a furnace residue. Since the structual formula for *Willemite* is $2ZnO.SiO_2$ and the corresponding formula for *Calamin* $2ZnO.SiO_2.H_2O$, and since, in the latter, the water and the silica are excluded from the reaction, here once more we have ZnO as the raw material of the process. With zincite, which is itself zinc oxide, and with Franklinite, in which the zinc is present as oxide, the same fact is, of course, obvious. It will be seen, therefore, that the production of zinc oxide always involves first the reduction of the oxide, ZnO, to metallic zinc, and secondly, the re-oxidation of this product to ZnO. As already stated, the sulphur dioxide from sphalerite is sometimes utilized as a by-product in the manufacture of sulphuric acid.

The residue after the removal of the zinc from Franklinite contains iron and manganese. This residue is further treated in blast furnaces to produce spiegel-eisen. This product runs from 19 to 21 per cent manganese, from 1 to 2 per cent silicon and under .08 per cent phosphorus. In the Bessemer process it is used as a recarburizer and for the introduction of manganese, as well as for special purposes in the open-hearth process and in foundry practice.

While the chemical reactions involved in the production of zinc oxide from its ores are simple and few, the physical chemistry of the oxide furnace is, on the other hand, a somewhat complex problem, and a correct understanding of it has a considerable bearing on the successful conduct of the process. The zinc being liberated in the form of vapor and combining with the oxygen while in this form, it follows that the oxide, when first formed is in a state of molecular division. The molecules of ZnO no doubt cohere more or less, into particles, as the oxide fume passes along the flues to the bag-room, and these particles in turn adhere again to form aggregates. The particles are, however, excessively minute and the aggregates are so loosely held together that they break down readily in the paint mill or the rubber compounding rolls. The volume of zinc oxide in comparison with its mass is remarkable. A barrel of the White Seal French Process oxide weighs 150 pounds, while the same volume of the solid oxide, zincite, would weigh about 2000 pounds. The extremely fine state of sub-division of the zinc oxide together with its chemical stability under the ordinary conditions of application form the basis of the valuable properties of this material.

Zinc oxide, like other metallic oxides, unites with oil acids, and more freely with resin acids, to form metallic soaps. This fact indicates to the paint manufacturer, not only for this oxide, but for all oxide pigments, the wisdom of selecting for his use, oils having low acid values and of resins properly and completely neutralized.

Application. By far the most important use of zinc oxide is in the manufacture of house paints and of enamels. For these purposes, its color, its high-tinting value and its great permanence, as well as its extreme fineness, admirably adapt it. It is the whitest of all available pigments and of all white pigments require the largest percentage of oil to fit it for use. In all the standard prepared paints it is largely used in percentages ranging from as low as 25 per cent to as high as 75 per cent, the proportion depending partly upon the individual preference or experience of the manufacturer, and partly upon the nature of the other pigments in the formula.

This adversity of practice is well illustrated in the following formulas, selected at random from the published analyses of typical prepared paints now in the market:

		Per Cent
1. Pigment.	Zinc oxide	60
	Basic carbonate white lead	40
Vehicle.	Linseed oil	89
	Dryer	11
2. Pigment.	Zinc oxide	45
	Basic carbonate white lead	27
	Basic sulphate white lead	12
	Asbestine	16

		Per Cent
Vehicle.	Linseed oil	88
	Turpentine dryer	12
3. Pigment.	Zinc oxide	42
	Basic sulphate white lead	41
	Calcium carbonate	5
	Silica	12
Vehicle.	Linseed oil	93
	Turpentine dryer	7
4. Pigment.	Zinc oxide	37
	Basic carbonate white lead	60
	Calcium carbonate	3
Vehicle.	Linseed oil	91
	Turpentine dryer	8
	Water.	1
5. Pigment.	Zinc oxide	43
	Basic sulphate white lead	37
	Barium sulphate	20
Vehicle.	Linseed oil	82
	Liquid dryer	17
	Water.	1
6. Pigment.	Zinc oxide	57
	Basic carbonate white lead	43
Vehicle.	Linseed oil	96
	Turpentine dryer	4
7. Pigment.	Zinc oxide	70
	Basic carbonate white lead	30
Vehicle.	Linseed oil	90
	Turpentine dryer	10
8. Pigment.	Zinc oxide	25
	Basic carbonate white lead	40
	Basic sulphate white lead	20
	Calcium carbonate	5
	Barium sulpahte	10
Vehicle.	Linseed oil	90
	Turpentine dryer	10

A long favored formula for a white tinting base contained one-third part of each of zinc oxide, basic carbonate white lead and barium sulphate. Another, which enjoyed for many years a high repute, was composed of 60 per cent zinc oxide and 40 per cent barium carbonate. Immigrant painters from Sweden and Norway have frequently stated that the standard outside white paint used in those countries is composed of zinc oxide and calcium carbonate in the proportion of 90 per cent and 10 per cent respectively.

A paint consisting of zinc oxide and linseed oil only dries with a hard

smooth surface. This fact has certain important advantages. The disadvantage is that when, in the course of years, the oil becomes dry and decomposed (as happens sooner or later with all paints) the paint coat cracks and peels off in patches. This makes it impossible to do a good job of repainting unless the old paint is burnt off or otherwise removed. White lead does not do this. When a white lead paint coat fails, it does so by crumbling to powder, or as painters say, "chalking." The surface of a chalking paint gives an even surface for repainting.

In a paint composed of zinc oxide and white lead, the advantages proper to each pigment are found. The zinc imparts whiteness, durability and permanence of color, the white lead enables the painter to get a good covering layer of paint with each coat applied and also insures a good surface for repainting, when in the course of time, the paint has perished.

Zinc oxide has an additional quality which is important. If two boards be painted, one with white lead and the other with zinc oxide, and exposed to a dusty atmosphere, the white lead board will accumulate dust much faster than the zinc oxide board. The smooth even surface of the latter makes it very difficult for the particles of dust to adhere, whilst the comparatively rough surface of the latter holds them. This is well shown when a wet sponge is passed over the board. The zinc board will show up white and clean, while the lead board will remain dirty.

A board painted with a mixed paint containing both zinc and lead, behaves, in this respect, like a board painted with straight zinc oxide. The latter, owing to its fine state of division, enters the glossy surface which the oil forms over the paint and imparts to the coating the same dirt-resisting (incidentally also the same moisture-repelling) power that a straight zinc oxide paint possesses.

The effect of this property on the protective value of the paint is obvious.

Zinc oxide is absolutely permanent in color, and in mixtures with lead retards or entirely prevents the discoloration of the latter by hydrogen sulphide.

For interior decorative paints zinc oxide is generally used in much higher percentages than in exterior paints, and not infrequently as a pure pigment. In flat wall paints it is combined with lithopone, both because of its pure color and because of its efficacy in minimizing the effect of light upon that pigment.

The higher grades of enamels contain no white pigment besides zinc oxide, the latter being usually a French process oxide.

The only precaution necessary to observe in the use of zinc oxide as a pigment is to keep the material dry and thus avoid its coherence into aggregates; to see that all resins entering into the formula with it are properly and completely neutralized; and to keep the mill as cool as practical during the grinding or mixing process.

The standard oxide of the paint manufacturers is the "XX" Black Brand, except for delicate tints, where the "Selected" is preferred. For the latter use, some manufacturers utilize a blend of "Selected" with "Red Seal" French Process Oxide.

For the manufacture of enamels the French Process oxides are preferred, especially the "White Seal" and the "Green Seal," the first-named yielding a somewhat smoother compound and requiring a smaller percentage of pigment to produce the same effect.

Zinc oxide is also largely used in the compounding of rubbers and special grades of oxide are manufactured for this industry.

In pharmaceutical preparations, toilet accessories, etc., the White and Green Seal French Process Oxides find rather extensive application.

Another important use is in linoleum and oil cloth manufacture, for which "Red Seal" French Process and "Selected" American process oxides are most in demand.

In the manufacture of printing inks, the French Process Oxides are the preferred material, as also in the manufacture of celluloid, white glue, white lead dressings, etc., where the "White" and "Green Seal" grades of this process are best adapted.

In the manufacture of paints the leaded oxides are used in the same way and for the same purpose as the New Jersey oxides.

The production of zinc oxide in the United States has increased from about 23,000 tons in 1890 to over 100,000 tons in 1917.

Consumption in the manufacture of paint and the painting industry has increased steadily from year to year, while, owing to the demands of the automobile industry, its use in the manufacture of rubber has shown a remarkable development within the past few years.

Leaded Zincs. A curious development, amounting to a revolution in the paint industry, has occurred during the period intervening between the publication of this chapter in its original form and the present revision. This revolution is directly due to the phenomenal growth of the rubber tire industry, dependent upon the steady increase in the use of automobiles.

Zinc oxide, after rubber and sulphur, is the most important ingredient of a high-grade rubber tire, representing a very considerable percentage of its total weight. For this use only the practically leadless oxides are satisfactory. As a consequence, there is an insistent demand from this industry for increased quantities of this class of oxides.

As pigments, on the other hand, the leaded oxides, for most purposes, are equally satisfactory and in some respect superior to the pure oxides. Consequently, notwithstanding the temporary inconvenience entailed by change in formulas, leaded oxides are rapidly and inevitably replacing the unleaded oxides in paint manufacture.

The several brands and grades of these so called "leaded zincs" as produced by the New Jersey Zinc Company, are as follows:

Standard, containing under 5 per cent basic lead sulphate.

Sterling averaging 10 per cent basic lead sulphate, with a high limit of about 13 per cent.

Superior averaging about 20 per cent, with high and low limits closely approximating 18 and 23 per cent.

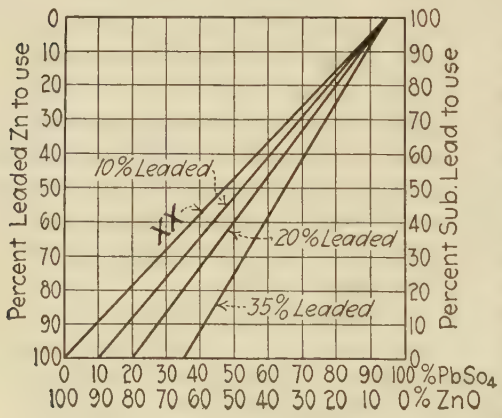
Lehigh, basic lead sulphate content closely approximating 35 per cent.

This last-named grade was developed to meet the demand of paint manufacturers for a high lead content. Its specific gravity is high in comparison with that of other oxides, about 5.9, as against about 5.7 for XX American, French process grades and Standard and Sterling leaded, and 5.8 for Superior leaded. This difference due to the lead content is also shown by the weight packed in the standard barrel, 400 lbs. for Superior and Lehigh, 350 lbs. for Sterling, as against 300 lbs. for other American process oxides.

The lead content of these oxides, as already indicated, is present in the form of the basic sulphate ($Pb_3S_2O_9 = 2PbSO_4, PbO$), though leaded oxides may be produced having practically the entire lead content in the form of the normal sulphate ($PbSO_4$). Such oxides are believed to be inferior in pigment quality.

In the manufacturing procedure these leaded oxides are usually ground with linseed oil to a paste having a thinner consistency than that of ordinary " white lead in oil," and this paste is used as a " base " for the manufacture of prepared paints.

The Lehigh grade, for example, when ground with 14 per cent its weight of oil, yields a paste paint of " lead in oil " consistency, suitable for use by painters following the usual routine procedure. Such a paste is admirable for admixture with ordinary white lead, the resultant paint


Percent Leaded Zn to use
Percent Sub. Lead to use
10% Leaded
20% Leaded
35% Leaded
XX
0 10 20 30 40 50 60 70 80 90 100 %PbSo4
100 90 80 70 60 50 40 30 20 10 0 % ZnO

The figures to the left indicate the percentages of Leaded Zinc and those to the right of Sublimed Lead required to produce the required percentages of ZnO and $PbSO_4$ indicated at the bottom of the chart. The four diagonal lines represent the several grades of oxide. To find any desired percentages shown in the bottom rows of figures, using any of the oxides shown, follow the perpendicular line to its interesction with the proper diagonal; the required percentages of that oxide and sublimed lead will then be found on the horizontal line to the left and right respetively. E.g., Desired percentages 50 each, using a 35 per cent Leaded Oxide. The 50–50 perpendicular intersects the 35 per cent diagonal at the horizontal line which indicates at the left, 76 per cent Leaded Zinc, and at the right, 24 per cent Sublimed White Lead. The desired percentages will, therefore, be obtained by using 76 lbs. of the former to 24 lbs. of the latter.

being virtually a three-pigment combination of basic carbonate, white lead, basic sulphate white lead and zinc oxide.

The paste used as a base for prepared paints is made by grinding about 100 lbs. of the oxide with 22 lbs. of oil. Such a base may be reduced to working consistency by somewhat less than 50 per cent by weight of additional oil, volatile thinners and dyers.

Rosin in any form is not to be recommended as a component of zinc oxide paints, but if present it should be completely neutralized. Oils low in acid number are preferable for grinding, and it is regarded as good practice to use about 10 per cent of turpentine in the vehicle.

In practice it is often desirable to make definite percentage combinations of leaded oxides with basic sulphate (sublimed) white lead. This latter product, as marketed, contains approximately 5 per cent of zinc oxide and the computation of formulas, using the leaded oxide, is a somewhat involved process. The chart on page 390 gives the required information at a glance.

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CHAPTER XV

PIGMENTS AND PAINT OILS

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Definitions. Paint consists of finely ground pigments mixed with suitable mediums and sufficient driers. Paint is used for decorative or protective purposes, and in most instances serves both ends. Enamels formerly embraced that class of paints composed of pigments ground in varnish which dried with a high gloss. Some objections were raised to this high gloss by consumers, who also demanded a semi-gloss finish and a flat or matte finish. A so-called "flat" enamel is really a misnomer, for the very word "enamel" indicates gloss. Driers are materials added to paints or enamels to make them dry properly. Their action is the same as that of a catalytic agent.

Historical. Painting as a decorative art can be traced back to very ancient times. We find that aborigines the world over decorated their persons with native earth colors. Some exhibited great skill in their use of the pigments, as is evidenced in the ruins of the temples of Luxor and Karnak in Egypt, where there are still decorative paintings to be found on the walls and on the pillars which are more than three thousand years old.

For decorative and preservative effect we find more evidence of the early use of paint in England than we do in any other country. There are items of expense in the reign of Edward I showing the use of paint about the royal buildings as early as the year 1274.

Up to the latter part of the fourteenth century oil painting for artistic purposes was not an exact art but was carried on more in the nature of experimentation. To Hubert and Jan Van Eyck, two Dutchmen, belong the credit of first having made public their manner of oil painting by means of pigments ground as near as we know in linseed oil. About 1400 the practice of oil painting had become thoroughly established, which can be attributed undoubtedly to the research and investigation of the Van Eycks. It is a fact worthy of mention that there is one painting in the National Art Gallery in the City of London by one of the brothers Van Eyck which is in as perfect a state of preservation as if it had been painted yesterday.

Application. Protective paint, by which is meant paint used for the purpose of protecting the surface to which it is applied, is relatively new, and it has only been within recent years that its value has been uni-

versally recognized. In Europe building construction is of such a character and is to a certain extent largely so to-day that paint is not generally used on the exterior of dwellings. Only in a pioneer country like America, where domiciles were made of wood, was it found necessary to apply an exterior coating to preserve the wood. Of course, time has wrought great changes in the character of homes in America as compared to the olden days. Engineering construction in all its phases, skyscrapers, bridges, tanks, etc., would last but a short time if it were not for the protection afforded by paint. In 1912 it was estimated that about one hundred million gallons of ready mixed paint were consumed in the United States, the general practice in this country being to purchase manufactured paints, for it is obvious that the paint manufacturer with his superior scientific knowledge and especially equipped factory with modern machinery can turn out paint far superior in quality to that made by hand by a painter who follows more or less empirical formulas.

Occasionally we hear a complaint made that the pigments manufactured nowadays are not as good as those that were made in former years and the poverty of the later day pigments is the cause of the early decay of many of our paintings. A belief of this kind is unfounded and needs correction, for the art of manufacturing colors has never reached a higher plane than it has at the present day. To the ignorance of the painters themselves and to the greed of some paint makers who adulterate and cheapen colors at the expense of permanency we should attribute the fugitiveness of our paintings. As nearly as can be determined, there existed between the twelfth and seventeenth centuries at most nine or ten pigments. To-day we have two hundred and fifteen or more, two hundred of which ought never to be used for permanent artistic painting.

When we see a painter with a pot of paint and a brush painting a wooden, brick, concrete or steel structure we imagine without further thought that that is the use to which most paints are put. As a matter of fact, paints and colors are also used in enormous quantities in the arts and sciences for other than decorative or protective purposes. A casual example showing the extent to which pigments are used in lines other than paint will be found in the list of purchases of the United States Bureau of Engraving and Printing, Washington, D. C., for the year 1910, when contracts were let for an annual consumption of 1,599,900 pounds of pigments, made up as follows:

White	802,200 pounds
Black	297,500 "
Blue	52,000 "
Green	180,000 "
Red	68,200 "
Yellow	200,000 "
	1,599,900 pounds

These pigments are identical in every respect with those used for general painting, and yet all these pigments were used for the purpose of printing the currency and the postage stamps of this Government.

The printing-ink industry in the United States consumes enormous amounts of paint materials. In some instances the material is ground in a varnish made of linseed oil, but for book and newspaper ink linseed oil is not used but resinous mediums which act as a binding material for the pigment.

The linoleum and oil cloth industries are also enormous users of paint in the strict sense of the word, and while it is true that the mixtures which they make differ from the house painter's mixtures the principle involved is identically the same as that covering ordinary paint.

The shoe and leather industries are users of paint materials in large quantities for making patent and harness leather, and so is the wall paper industry, the window shade industry, the rubber industry and the cement industry—all using for their color effects the same pigments that are used for ordinary painting.

Strictly speaking, paint which is used on brick, concrete, steel or wood is an engineering material and serves a purpose which is far more valuable than we imagine offhand.

A general description of the materials entering into the ordinary general manufacture of paint follows.

PIGMENTS

White Pigments

White Lead. White lead is the oldest of all white pigments and will be found described as far back as 400 B.C. by Pliny. White lead was made from the mineral Cerusite, which is a native carbonate of lead, but about 400 years ago the Dutch found that when pig lead was submitted to the action of carbonic gas from rotted tan bark and manure in the presence of vinegar the basic acid salt which was first formed was slowly converted into a hydrated carbonate of lead. This same method is used to this day, but newer methods are also used such as the precipitation of hydrated carbonate of lead from a solution of lead by means of carbon dioxide. White lead makes an excellent paint, particularly when added to other materials such as inert fillers and other pigments. White lead is affected by sulphur gases, as the lead sulphide formed is of a dark brownish color. For this reason white lead paint should not be used around stables, out-houses, etc. White lead paint gives a rather soft film, and a zinc oxide paint a hard film, so that a happy medium is struck when a paint is made containing a mixture of white lead and zinc oxide as the pigment.

Lead Sulphate. Lead sulphate has very little value as a paint material owing to the fact that sublimed white lead supersedes it.

Sublimed White Lead. Sublimed white lead is a furnace product made from the sublimation at a very high temperature of Galena. It is an amorphous white pigment, very uniform and fine in grain. Within the past decade it has come into great prominence among paint makers, it now being regarded as a stable, uniform and valuable paint pigment. When mixed with other pigments, such as zinc oxide, carbonate of lead and the proper reducing materials added, such as silica, clay, barium sulphate, etc., it produces an excellent paint whose wearing qualities at the seashore are superior to that of carbonate of lead. The composition of sublimed white lead might be stated as being 75 per cent lead sulphate, 20 per cent lead oxide and 5 per cent zinc oxide, although each of these figures will vary slightly either way. It has been stated that sublimed lead is not as susceptible to sulphur gases as white lead, but while it may take hydrogen sulphide a longer time to discolor it, it is simply a question of degree and it is acted upon by sulphur gases, although not as quickly as white lead.

Standard Zinc Lead White. This material contains approximately 50 per cent of lead sulphate and 50 per cent of zinc oxide. It has been superseded by a material known as Ozark White, which is made by the Ozark Smelting and Refining Company of Missouri. The latter pigment contains about 60 per cent zinc oxide and 40 per cent lead sulphate.

Ozark White. Ozark White is a very desirable pigment and has all of the good qualities of Standard Zinc Lead White and Sublimed White Lead. It consists of approximately 60 per cent zinc oxide and 40 per cent of lead sulphate.

Zinc Oxide. Zinc oxide is one of the most widely used pigments and is made by subliming the metal and also zinc ores. It is erroneously believed that zinc oxide is not affected by sulphur gases and therefore will not turn color. Zinc oxide is acted upon by sulphur gases, but not visibly, as zinc sulphide, zinc sulphite and zinc sulphate which may be formed are white, and therefore the reaction is not evident to the eye. Zinc oxide paint produces a rather hard film and white lead a soft film, so that a mixture of zinc oxide and white lead in the proper proportions forms an admirable paint. Zinc oxide is also largely used in enamel paints.

Zinox. This is a hydrated oxide of zinc. It is not made in this country but manufactured and used almost entirely in France. It is generally sold either in a semi-paste form or in the form of a ready mixed enamel. It possesses about the same qualities as zinc oxide, although it is claimed that it possesses a slight advantage over zinc oxide in that it remains in suspension longer than any other pigment. This is problematical.

Lithopone. Lithopone consists theoretically of 29½ per cent zinc sulphide and 70½ per cent barium sulphate. It is made by mixing solu-

tions of zinc sulphate and barium sulphide in molecular proportions in accordance with the following reaction:

$$ZnSO_4 + Aq + BaS + Aq = ZnS + BaSO_4 + H_2O.$$

The precipitate formed has no body or hiding power and requires very careful manipulation in order to convert it into a suitable pigment. However, when washed, dried, heated to dull redness, suddenly plunged into water, ground in its pulp state and washed and dried again it makes an excellent paint pigment. It is a brilliant white, extremely fine in texture and has excellent hiding power, having more hiding power than pure zinc oxide. It is stable in every medium known for paint purposes excepting those which are highly acid. Lithopone is largely used for flat wall paints and also in the cheaper grades of enamel paints. As an interior white, a first coat white, or as a pigment in the lighter shades of floor paints lithopone cannot be excelled for its body, durability, hardness, fineness of grain and ease of application. It does not oxidize progressively, and this feature has made it of inestimable value to the table and floor oil cloth industry. Lithopone has the peculiar faculty of darkening in the sunlight, but when night comes a change takes place and the next morning it will be as white as it ever was. This is called the "photogenic" quality. This action goes on continually.

Oxides of Lead

Litharge. Litharge is the first oxide of lead, having the formula PbO. It is yellow in color. Litharge has excellent protective qualities, because it is basic and therefore resists corrosion. Care has to be exercised in its use, as it combines with linseed oil so rapidly that when used in mixed paints to any great extent it tends to "liver" and saponify. Flake litharge is generally used by varnish makers or oil boilers for making drying oils.

Red Lead. Red lead is a very heavy orange-red pigment more or less crystalline in structure. It is made by heating litharge to a temperature of 600° to 700° F. It is used to a very large extent for priming structural steel. When prepared in linseed oil it must be freshly used, otherwise it will form a distinct combination with linseed oil and become hard and unfit for use. Once set it may be reground but will never set again. Red lead is also put on the market now in a semi-paste form, materials being added to keep it in a soft condition until used.

Blue Lead. Blue lead is formed in the sublimation of Galena. It is of a bluish gray color. As a priming coat it has been well spoken of.

Red Pigments

Venetian Red. Venetian red is a ferric oxide containing gypsum, the composition being 20 to 40 per cent ferric oxide and 60 to 80 per cent

calcium sulphate. It is usually made by heating ferrous sulphate in the presence of lime. This pigment has been known for upwards of a century.

Indian Red. The Indian red originally used was a native oxide of iron. The Indian red of commerce, however, is an artificial product made by calcining copperas. There is no pigment, with possibly the exception of lithopone and artificial barium sulphate, which will approach Indian red in fineness of grain. Indian red is not only used as a pigment but also for polishing gold, silver and other metals.

Quicksilver Vermilion. Quicksilver vermilion is the amorphous mercury sulphide which is normally black, but when made with sulphur in the presence of an alkaline solution it becomes bright red. It has the disadvantage of darkening in the light and eventually turning brown.

Permanent Vermilion. Permanent Vermilion is usually orange mineral tinted with paranitraniline. Enormous quantities of this pigment are used. It has great tinctorial strength.

Helio Fast Red. Helio fast red is of the vermilion type. It is also known as Harrison red. It is made from nitro-paratoluidine, and in tinctorial strength is practically ten times stronger than quicksilver vermilion. It is, however, a bad drier. When used in sufficient strength it is permanent, but if diluted to too great an extent the base upon which it is made masks the pigment.

Lithol Red. Lithol red has the advantage over paranitranilines in that it does not bleed and that it does not turn dark upon exposure. It is, however, largely used for a permanent red for railway signals. When not reduced or diluted with too much clay and barytes it is permanent, but when it contains an excess of so-called reinforcing pigments it washes out and fades.

Brown Pigments

Burnt Sienna. This is a permanent reddish brown pigment made by calcining raw sienna, raw sienna being a hydrated oxide of iron containing clay. The ferric oxide content in the American grade ranges from 25 to 60 per cent, depending upon the original ore while in the Italian burnt sienna the ferric oxide content averages from 60 to 75 per cent. Siennas have staining power rather than hiding power.

Burnt Umber. Burnt umber is made by calcining raw umber, which is a native earth found in Italy, Greece and Turkey. All umbers normally contain over 5 per cent of manganese dioxide, while some of them contain as high as 20 per cent manganese. The remainder is largely ferric oxide. Umber is really a clay earth stained with oxides of manganese and iron.

Burnt Ochre. Burnt ochre is made by calcining the native ochre, which is hydrated oxide of iron and clay ore, until the ferrous salt is converted into ferric. Paint containing burnt ochre as pigment will cover solidly.

Prince's Metallic or Princess Mineral Brown. This pigment is mined in the United States, and was named after a man, Prince, who originally mined and marketed it. It is used to a very large extent in roof and freight car paints.

Van Dyke Brown. Van Dyke brown is a native earth, being a clay earth stained with a bituminous compound. It is used in mixed paints, principally on account of its deep shade and translucent appearance.

Yellow Pigments

Ochre. Ochre is clay stained with the hydrated oxide of iron. The French ochres are more brilliant than the American ochres.

Chrome Yellow. Chrome yellow is a lead chromate of medium shade as precipitated from a solution of nitrate of lead and potassium bichromate. The lighter shades are made from solutions acidified with organic or inorganic acids. Chrome yellows when thoroughly washed are permanent to light, but they cannot be used where sulphur vapor is generated as lead sulphide is formed, which reduces the brilliancy of the color.

Chromate of Zinc. This material is used to some extent by artistic painters. It is soluble in water to a large degree and therefore should not be used as a finishing coat for commercial work. It is used to a considerable extent in interior and flat wall paints.

Blue Pigments

Ultramarine Blue. Ultramarine blue, whether artificial or genuine, is chemically the same. Natural ultramarine blue is known as lapis lazuli. The only advantage that the natural has over the artificial is that it is not affected as quickly by acids as the artificial is.

Artificial Cobalt Blue. The cobalt blue of commerce is the same as ultramarine blue, the difference being in the shade. Chemically it is about the same as ultramarine blue.

Prussian Blue. Prussian blue is a ferri-ferro cyanide of iron. There are a number of varieties of Prussian blue, all approximating the same composition, though slightly different in shade. They are made differently, and are known as Steel Blue, Milori Blue, Bronze Blue, Antwerp Blue, Chinese Blue and Paris Blue. If Prussian blue is free from soluble salts it is a stable color and will not change shade.

Green Pigments

Chrome Green. Chrome green is principally a mixture of Prussian blue and chrome yellow. When chrome green is used as a pigment it should be free from soluble salts, otherwise the soluble salts are liable to affect the linseed oil. A paint which contains chrome green when used at the seashore usually bleaches, so that a paint for that purpose should contain chromium oxide as the pigment.

Chromium Oxide. Chromium oxide is the only perfectly permanent green made. It mixes with every other pigment without decomposition and stands exposure to light without fading or darkening. It is unaffected by alkali.

Green Aniline Lakes. Those green aniline lakes which are alkali-proof are very largely used in flat wall paints, as extreme permanence to light is not necessary since these paints are used for interior work. These lakes are used only as tints, as they do not possess hiding power.

Zinc Green. Zinc Greens are usually mixtures of chromate of zinc and Prussian blue and are extremely brilliant and permanent to light, but not permanent to alkali or water. They are largely used in flat wall paints and for paints for interior decoration.

Verte Antique (Copper Green). This is generally bicarbonate of copper. It is used for producing a corroded copper effect, known as verte antique.

Black Pigments

Lampblack and Carbon Black. Both of these are condensed soots, the one made from dead oil, and the other usually from gas. They are pure carbon.

Graphite. Graphite is either artificial or natural, and very seldom contains more than 60 per cent of carbon. It has a peculiar silvery luster by which it can be identified.

Charcoal and Coal. Charcoal and coal are analogous in composition, except that charcoal black is alkaline and coal black acid.

Vine Black. Vine black, in all essentials, is the same as the powdered charcoals for paint purposes, excepting that the grain is smaller and the black denser.

Ivory Black. Ivory black is still used to some extent for very intense coach colors, and there is also a very fine species of carbon black on the market known as the "Extract of Ivory Black," which is made by digesting charred ivory chips in hydrochloric acid until nearly all of the calcium phosphate is dissolved. Such a black has intense staining power and is by the far the blackest material made. It is very expensive, colloidal in its nature, and used therefore for ready prepared color-in-varnish or high grade black enamels.

Drop Black. Drop black is generally made by calcining sheep bones, which are then impalpably ground in water, and when in paste form cast into small drops; hence its name, "Drop Black."

Black Toner. Black toners may be either the extract of ivory black, the extract of bone black, or certain forms of carbon black, or carbon black upon which nigrosine has been precipitated.

Benzol Black. Benzol black is a carbon black which, however, is much better than the carbon black produced from natural gas. It is

soft, contains no granular particles, and remains in suspension for many weeks in both oil and varnish. It is, however, a very poor drier, like most of these blacks, and therefore a mixture of litharge and red lead oil is recommended when they are to be used.

Acetylene Black. This black is not quite as common as it was some years ago. It has very desirable properties and can be used for tinting purposes without showing granules or streaks, as is often the case with carbon black made from gas. It is flocculent and somewhat colloidal in nature.

Mineral Black. Mineral black is usually a slate colored with oxide or iron.

Inert Fillers and Extenders

These materials, which at times have been called the "re-enforcing pigments," have their value when used in moderate proportions, and yet it is not within the province of any paint chemist to say to what extent these materials can be classed as adulterants and to what extent they can be classed as inert fillers or re-enforcing pigments. In every case where this question comes up common sense, judgment, and best practice provide the answer.

Barium Sulphate. Barium sulphate is an artificial precipitate, usually made from barium chloride and sodium sulphate, and is largely used as a lake base, and in its dry form as a re-enforcing pigment. The United States Navy has lately adopted it in a very large way for making battleship gray.

Barytes. Barytes has the same chemical composition as the artificial barium sulphate, but is the native mineral, finely powdered.

Barium Carbonate. This material is practically new as a paint material. Under the microscope it has a very peculiar structure. It is not made by mixing a solution of barium chloride and sodium carbonate, although that would be the normal way of making it, but it is made from barium sulphide and sodium carbonate in fairly concentrated solutions, so that the sodium sulphide becomes a valuable by-product, and therefore the barium carbonate can be successfully marketed at a reasonable price.

Silica and Infusorial Earth. Silica and infusorial earth are usually either ground quartz or the native infusorial earth washed and powdered. China clay and kaolin are silicates of alumina largely used as either re-enforcing pigments or substratums for lakes.

Asbestine and Asbestos. Asbestine and asbestos are silicates of magnesia, the asbestine having a short fiber and the asbestos having a long fiber. Asbestos fiber is used to a small extent in paint, but it is not as good as asbestine, because the fiber of asbestos is too long. However, considerable quantities of asbestos are used for the making of so-called "fire-proof" paints.

Calcium Carbonate. Calcium carbonate is either whiting, or white mineral filler or powdered marble.

Gypsum and Terra Alba. Gypsum and terra alba are either artificial or natural calcium sulphate.

Paint Vehicles

The vehicles or liquids used in making paint are linseed oil, soya bean oil, China wood oil, fish oil, corn oil, pine oil, turpentine, benzine, benzol, turpentine substitutes and driers.

Linseed Oil. Linseed oil is the oldest paint vehicle known. It is the oil expressed from the flax seed. It was formerly known as linnen seed, hence its name, linseed. Most of the raw linseed oil produced in the United States comes from the Northwest. The foreign oils come from Calcutta, the Baltic, and the Argentine regions. The oldest method for extracting the oil consists in crushing the seeds, heating it in a steam-jacketed kettle and finally subjecting it to hydraulic pressure. In a later method, which is a continuous one, the crushed seed is forced through a screw press, the oil thus oozing through the openings in the bottom of the tube while the cake falls out at the end in the form of flakes. A third process consists in extracting the crushed seed by means of naphtha, the excess of solvent being subsequently removed by evaporation.

Linseed oil dries by oxidation and this may be hastened by the addition of salts of lead or manganese, known as driers.

Soya Bean Oil. Soya bean oil is closely allied to linseed oil, but there are some seventeen varieties of it, and most of them are very poor driers, and remain sticky for a long time. There are three or four varieties of soya bean which yield very good oil, but until these are scientifically cultivated it will be rather difficult to recommend them.

China Wood Oil. China wood oil has been known in America since 1896 only, and is known under the name of tung oil, kiri oil, and China nut oil. It cannot be used in its raw state, but must always be cooked, with the addition of a suitable drier, to a temperature of over 500° F. It makes a very waterproof material.

Fish Oil. There is only one variety of fish oil that is used in paint making, and that is known as menhaden fish oil, which is the oil extracted from the moss-bunker. The fish are collected on the northeastern coast of North America. When used up to about 70 per cent with other oils, it makes a suitable oil for paint purposes.

Corn Oil. Corn oil, as the name indicates, is the oil pressed from the seed of the corn or maize plant, and does not dry very well. When mixed with linseed oil it has some uses as a grinding oil.

Pine Oil. The term "pine oil" as now understood, is the heavy oil obtained from the fractionation of crude steam-distilled wood turpentine. When the sap of the pine tree is subjected to distillation in a current of

steam the volatile liquid—turpentine—consists almost entirely of the hydrocarbon, pinene ($C_{10}H_{16}$). When, however, the trunk, stumps, and roots of the same tree have been allowed to remain on the ground for a number of years and are then steam distilled, there are obtained, in addition to the turpentine and rosin, certain heavier oils formed by hydrolysis and oxidation as a result of exposure to the atmosphere. To the heavier oils thus formed and yielded up to the process of steam distillation the term " pine oil " is properly applied.

Turpentine. Turpentine is one of the oldest solvents known. It is collected from the sap of the pine tree in the southern part of the United States and when the sap is distilled it yields ordinary rosin and spirits of turpentine.

Benzine. Benzine is a light fraction of petroleum oil or asphalt oil, and is more inflammable than turpentine. It has a very large use in the paint industry, particularly for the manufacture of oil cloth, linoleum, etc., where a cheaper solvent is necessary.

Benzol. Benzol is a light fraction derived from coal tar and has great solvent properties. It is a desirable constituent of mixed paint which is to be used for painting new wood, and if used up to a reasonable limit improves the spreading quality of paint considerably.

Turpentine Substitutes. There is a large class of turpentine substitutes which are replacing turpentine itself. These are the higher fractions of petroleum and asphalt oils which have about the same specific gravity as turpentine. They are much more reasonable in price, and in many instances serve the purpose of pure turpentine.

Driers. Driers are needed in almost all paints. It is assumed that they exert no chemical action but attract oxygen from the air by virtue of their presence. The principal driers used in paint making are made of soaps composed of lead and manganese in some form or other, usually as the linoleate or the resinate. Too much drier is regarded as harmful in paint, but a limited amount serves a very good purpose in that the paint is made to dry before dust can collect.

Lakes are dyes precipitated on a transparent base and are more or less transparent or translucent. There are two kinds of lakes, those made from the aniline dyes and those made from the wood dyes. An example of an aniline lake is Scarlet Lake, used in printing ink, which is made by dissolving a dye like 2R Scarlet in hot water, mixing the water with blanc fixe, alumina, clay or a mixture of these bases and then precipitating the color by means of barium chloride. Some dyes are precipitated by means of tannic acid, others by means of lead salts and still others by means of barium salts. The wood extracts like Persian Berry, Quercitron and Hypernic lake are generally precipitated by means of tin chloride, and they are not as fast to light or as brilliant as the aniline lakes.

No general rule can be given for the manufacture of a lake for every

mordant and every base has a different influence on the shade of the color. A yellowish scarlet, for instance, is turned bluish when zinc and lime salts are used. A lake which ordinarily is very transparent becomes opaque when a base like carbonate of barium is used. There is very little written on the manufacture of lakes for the reason that this subject is largely empirical and every manufacturer has formulæ of his own which are slight variations and modifications from the recognized methods.

CHAPTER XVI

THE MANUFACTURE AND USE OF PREPARED PAINT PRODUCTS

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Conditions Responsible for the Introduction of Prepared Paints. Paint making thirty or forty years ago was conducted upon a rather

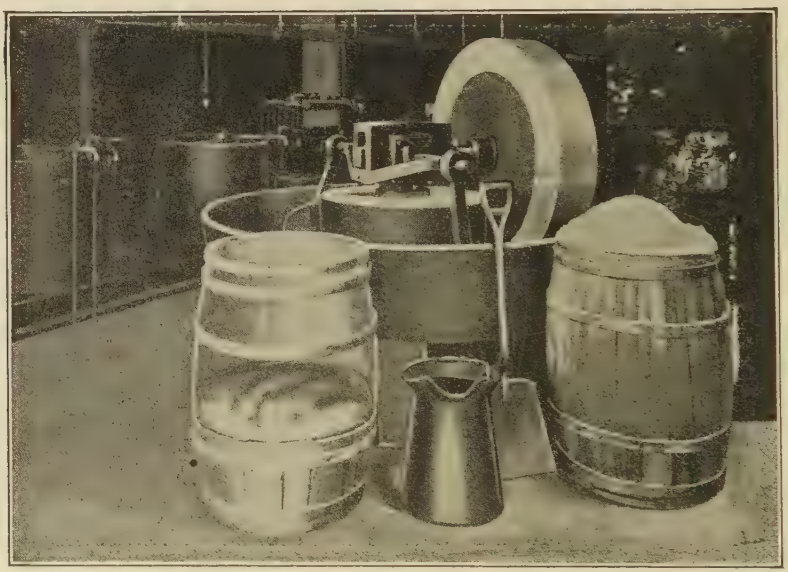

FIG. 182.—Illustration showing the condensing action of milling pigments with oil. The full barrel of pigment at the right, produces a barrel one-third full of paint, when milled with oil.

crude and empirical scale. Painters' apprentice boys, laboriously and often without great care, stirred their white lead paint base, with oils and thinners, in tubs and barrels. Tinting colors, ground in small quantities with slab and hand muller, were added. The production of a few gallons of lumpy and half-mixed paint was the result of many hours' work. Considerable waste attended the preparation of such paints, as the amount prepared for a certain job was often actually greater than required, the balance being allowed to remain in uncovered kegs where it would

soon become hard and unfit for further use. The difficulty often experienced in duplicating certain mixes or matching certain tints was aggravated by the troubles experienced with impure or adulterated raw materials. The disappearance of the apprentice system and the attending difficulty of obtaining journeymen or foremen qualified to produce the proper shades and tints for various types of work added to the problem. The maintenance of vast properties, such as our great modern railroad systems, which use standard colors on their buildings and equipment, and the enormous office buildings in metropolitan centers requiring thousands of gallons of paints and other finishes, necessitated the use of machine-made prepared paints. All these conditions were factors in bringing about a gradual change in the painting trade. The greatest factor, however, was the growing conviction among painters that the white lead paint produced by hand mixing could not be used successfully for all types of work, and that certain other pigments, then gradually coming into use, gave to the white lead, properties which enormously increased its value for certain purposes.

Growth of Industry Caused by the Introduction of Science into Paint Making. The first attempt to produce prepared paints in this country did not meet with great success; the lack of technical knowledge regarding the properies of pigments, oils and colors, which then existed, in many instances being responsible for the low type of product first produced and for the consequent prejudice created against the use of paints in prepared form. These conditions, however, soon changed, and with the introduction of laboratories under the supervision of trained chemists, the manufacture of prepared paints rapidly developed into an industry in which the processes were controlled by the application of scientific principles and in which the raw materials used were most carefully examined for their chemical purity and physical properties. To-day the manufacture of prepared paint products in the United States constitutes one of the most important industries of the country, aggregating, as it does, the production of over one hundred million gallons annually and exceeding in value Germany's much vaunted coal tar dye industry. Thousands of different kinds of ores, chemicals, oils, gums, resins, volatile thinners, and other materials are employed in the manufacture of these products, and the skill of the chemist is applied to a great extent in the examination and utilization of these raw products. The more generally used of these products will be discussed under separate headings. It is, of course, impossible to present a description of several hundred different kinds of prepared products which are being made and used for specific purposes, and only the most important will therefore be described.

Materials from which Paints are Made. Raw linseed oil is used as the vehicle or pigment carrier for the majority of paints. When spread in a thin layer, this oil absorbs large quantities of oxygen from the air, becoming solidified to a rubber-like mass.

Modern research has demonstrated the value of other oils also, notably perilla oil, which is already being used with great success. The addition of pigments to the oil effects the formation of much stronger films and at the same time provides opacity and color, the oil-pigment film hiding and decorating the surface to which it is applied. When rapid drying paints are required, liquid driers are added, which accelerate the drying of the oil. These driers are prepared by dissolving in hot oil, considerable quantities of active oxygen-carrying substances, such as the oxides of lead and manganese, subsequently thinning the mixture with turpentine and benzine in order to reduce its consistency. Cheaper forms of drier, to be used in certain types of paint, are prepared by hardening rosin with lime and lead oxide, and reducing the resinate with benzine or other volatile liquid. Such a drier is generally called gloss oil. Boiled linseed oil, which is used in paints that are required to dry rapidly to a glossy surface, is produced by heating raw linseed oil to a very high temperature and incorporating at such temperatures small percentages of metallic oxides. Turpentine, high boiling point petroleum benzine, and coal tar benzol are added to paints to thin them to a suitable consistency for application. These thinners have the effect of causing paints to penetrate into the pores of wooden surfaces on which they may be used. The thinner, of course, volatilizes during the drying of the paint. Varnishes are also used to a considerable extent in the preparation of some types of prepared paints. Varnishes are prepared by fusing fossil resins, such as kauri and copal, combining the fused product with hot oil, and reducing the mixture with turpentine. The white pigments used in paints are either of the opaque type, such as basic carbonate-white lead, basic sulphate-white lead, zinc oxide, leaded zinc, and lithopone, or of the transparent type such as barytes, china clay, silica, asbestine, etc. The color pigments used are natural earth colors and chemically precipitated colors, either of organic or inorganic origin.

Factory Arrangements. The dry pigments are usually kept on the top floor of the factory, in bins or barrels. Provision is made on the same floor to dump weighed amounts of the various pigments into the mixers on the floor below. The liquids, such as oil, turpentine etc., which are used in the manufacture of paints, are generally stored in large steel tanks which are kept in the basement or outside of the factory. By pressure the liquids are forced to different parts of the factory where they may be required. The pipes in which the liquids are contained are painted different colors in order to differentiate between the liquids. The pipes are generally connected to gauging machines so arranged that definite quantities of oil or other thinners may be rapidly drawn at any point where required.

Making Prepared House Paints. In the manufacture of prepared house paints, the pigments to be used are weighed out in the proper proportions. Linseed oil is placed in large rotary mixers, the pigment

added and the mass thoroughly agitated. For the grinding of lead and zinc pigments which are to be used in special paints, the pigment and oil mixture is sometimes placed in the bed of a large chaser where it is heavily kneaded with a large revolving roller. The kneading, effects a dense paste containing a small percentage of oil and therefore very opaque in nature. The oil-pigment mix is then milled through revolving plates of dressed stone or steel, issuing forth as a smooth, heavy paste. From

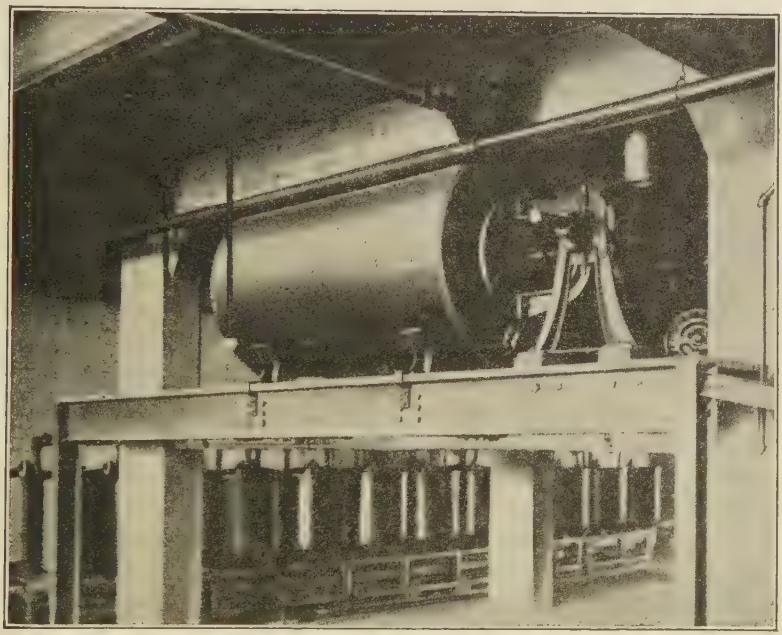

Fig. 183.—Horizontal Paste Mixer.

the grinding mills this mixed pigment paste is allowed to flow into large storage tanks where it is kept in semi-paste condition. When desired, a quantity of the paste is removed to a smaller tank called a mixing or shading tank, where the paste is thinned with a certain definite amount of linseed oil. Turpentine, thinner and liquid drier are added to make the paint more liquid and suitable for immediate use. Tinting colors, ground in linseed oil, are also added if the paint is to be colored. After thorough stirring, the prepared paint is packed in containers which are subsequently closed, labelled, and boxed for shipment.

Composition of Prepared House Paints. Prepared house paints usually contain approximately 65 parts by weight of pigment and 35 parts by weight of vehicle. The vehicle of high grade paints is pure linseed oil with a small percentage of turpentine and liquid drier. The pigment portion consists of a mixture of the white lead pigments and zinc oxide, sometimes containing a moderate percentage of inert pigments

such as barytes, asbestine, silica, whiting, gypsum or china clay. The cheaper paints contain a much larger percentage of the inert pigments and a minor proportion of the opaque white metallic pigments. The coloring matters used for tinting are varied and consist of natural earth colors, such as sienna, umber, ochre or iron oxide, or chemically prepared pigments such as lead chromate, Prussian blue, chrome green, carbon black, etc. The paint maker has a wide range of such colors from which to choose and can therefore produce paints of practically any desired tint or shade.

Durability of Paints for Wooden Surfaces. Exterior exposure tests have been made in many sections of the United States, to determine what types of paints are best suited for the protection of wooden surfaces. In every instance, these tests have been conducted and reported upon by various scientific societies and educational institutions. The results of the tests have proved that single pigment paints, such as corroded white lead in oil, do not give entirely satisfactory results. Paints made of the white lead pigments (corroded or sublimed) combined with zinc oxide, with or without a moderate percentage of inert pigments such as barytes, silica, asbestine, etc., have given the best results from the standpoint of durability and color maintenance. The tinted paints have proved most satisfactory in this respect, the effect of the color in promoting the life of a paint being very pronounced.

Barn Paints. In agricultural districts where there are many barns and similar out-buildings to paint, there is a wide demand for the so-called "barn paints" which are usually made of the cheaper grades of iron oxide ground in linseed oil or mixed oils and thinned with benzine. Gloss oil driers made from rosin treated with litharge and dissolved in benzine, are occasionally added to accelerate the drying of such paints. The higher grades of barn paints, however, are made with linseed oil and turpentine driers. Some agriculturalists prefer to use the best and most expensive grades of prepared house paints upon all their out-buildings, thus obtaining the most satisfactory and economical results.

Enamel Paints. A desire for gloss coatings of great brilliancy and light-reflecting value, for the interior woodwork of dwellings, has led to the manufacture of special paints of this sort, which are popularly known as enamels. These were at first produced by dissolving white damar gum in turpentine and using this liquid as the vehicle in which to grind the pigment base, which was generally composed of French process zinc oxide used in sufficient quantity to give an enamel of good body. When applied to a surface, such enamels would dry rapidly to a high gloss. Higher grade enamels were made of French process zinc oxide ground in short oil varnishes of the copal type. More recently, however, lithopone has been used in place of zinc oxide for the production of certain types of enamel. Bodied oils are also finding a wide application as a vehicle for such products. Linseed oil, blown and bodied to a very heavy consistency, forms an excel-

lent enamel vehicle especially when mixed with a light hard resin varnish. Enamel paints produced through the use of such oil are more durable for exterior purposes than those produced from straight spirit or gum varnishes. In the manufacture of some enamels the pigment base is often milled in a very small amount of bleached linseed oil, in order to condense it as much as possible, the paste being reduced with boiled oil and run through roller mills, subsequently to be thinned with a light turpentine oleo-resinous varnish. Zinc and lithopone enamels have almost entirely replaced the use of corroded white lead for interior painting work. As a ground coat for these enamels, there is generally applied a paint made of lithopone ground in a vehicle which will dry very flat. The application of the enamel over the flat coating produces a very brilliant and durable finish.

Flat Wall Paints. The application of paints to the interior walls and ceilings of dwellings, office-buildings and other public structures, is rapidly becoming universal. This is in part due to the general recognition of the fact that the public health must be guarded by providing and maintaining the most sanitary conditions wherever people are confined for any period of time. It is obvious that the use of wall paper for interior decoration works directly against the fundamental principles of hygiene. The easily decomposable starch or glue binder in wall paper forms an excellent culture medium for bacilli, while its rough and unwashable surface collects and retains the dust which may be present in any room. Interiors should be made sanitary through the use of durable paints designed to provide a maximum degree of service. That the use of paints for this purpose constitutes a great aid in the modern effort to provide the most sanitary and healthful conditions, is evident when we take into consideration the fact that during the drying of oil paints, aldehydic substances are evolved which are destroyers of pathogenic bacteria; newly painted surfaces being practically free from bacilli.

During the past few years there have appeared on the market a number of washable wall paints composed of non-poisonous pigments ground in vehicles having most valuable water-proof qualities. When spread, these paints dry to a flat, semi-flat or matt finish which has become very popular on account of its restful effect upon the eyes. These products, which are called Sanitary Flat Wall Paints, are composed of lithopone and zinc oxide admixed sometimes with small percentages of the more inert pigments. The pigments are ground in special flat varnish liquids made from treated tung oil, thinned with high boiling-point petroleum thinners. In some of these paints there is used a very heavy bodied linseed oil which increases the binding properties of the paint. The remarkable hiding power of lithopone, the pigment generally used in making these paints, is responsible for their economy in use—one or two coats being sufficient to do the work which formerly required several coats of flatted white lead paint. Flat Wall Paints are produced in many

shades and tints, the lighter colors being most suitable for the walls of school rooms and hospitals, while the darker colors are generally preferred for living rooms and libraries.

Factory Paints. In order to brighten the interiors of factories, and thus increase the amount of illumination and working efficiency of the employees, the walls and ceilings are generally coated with white or light tinted paints. These are usually made on a lithopone base, the vehicle being treated tung oil or linseed oil. A considerable quantity of turpentine or similar thinner is generally used to produce a flat surface. For a gloss surface, the lower priced grades of zinc and lithopone enamels are used.

Cement Paints. Portland cement, on account of its adaptability to the principles of re-enforcement, is being used extensively for the construction of buildings of all types. The desire to decorate the rather unpleasing appearance of cement structures and at the same time render them waterproof has created a demand for paint coatings suitable for this purpose. High-grade prepared house paints have proved suitable in many instances. Specially prepared cement paints have also given excellent results and are being widely used for this purpose. Their composition generally shows the presence of sublimed or corroded white lead, zinc oxide or lithopone as a base pigment, combined with a considerable percentage of inert pigment and ground in highly waterproof vehicles prepared from treated tung oil. When such paints are to be applied to freshly laid damp cement or concrete construction, the surface of the concrete is generally washed with a solution prepared by dissolving zinc sulphate crystals in water. This solution neutralizes all the calcium hydrate present in the surface of the cement.

Metal Paints. Iron sheets or other forms of iron and steel, if left unprotected, will corrode in a very short time. If properly protected by paints, they will remain for years in a perfect state of preservation. Prepared paints are now being used in enormous quantities for this purpose, thus preventing corrosion and effecting annually a saving of many million dollars.

The corrosion of iron is due largely to a form of electrolysis which takes place in the presence of moisture and air. Impurities which are generally segregated throughout the metal, may become electronegative to iron, and in the presence of moisture excite galvanic action which causes the more electro-positive metal (the iron) to go into solution and form rust. This effect may be prevented by placing on the surface of the metal substances which make the iron passive to electrolysis. Soluble chromates and alkalies, or basic substances, have this effect. If chromate pigments or basic pigments are used in paint coatings, their effect when applied to metal is to render the iron passive and thus prevent electrolysis and corrosion. Zinc chromate and basic chromate of lead (American vermilion) are prominent examples of rust inhibitive pigments

of the chromate type. Basic sulphate of lead (sublimed blue lead) and zinc oxide are prominent examples of basic rust inhibitive pigments. These pigments are used in combination with the more inert or neutral pigments such as iron oxide and silica, as the pigment portion of metal paints. They are ground in raw linseed oil with a small proportion of thinner and drier. Sometimes heavy mixing varnish is added in small quantity, in order to make the paint coating more impervious to moisture and the gases of the atmosphere, which have corrosive tendencies. Red lead which contains 85 per cent of Pb_3O_4 and 15 per cent of litharge is very basic on account of its litharge content. Such red lead is highly in favor, as the pigment to use in the first or priming coat for metal surfaces. This type of red lead is sometimes mixed with an equal proportion of asbestine and ground in linseed oil to form prepared red lead paints. When such paints are used, they give excellent results, especially when they are subsequently coated with rust inhibitive prepared paints such as have been previously referred to.

Bituminous Paints. Water pipes and carriers which are to be buried in the ground; cement masonry below the surface of the earth, which is subjected to hydrostatic pressure; various forms of tunnel structures which are subject to very moist conditions; and similar types of heavy metal, generally require a very thick protective coating. For this purpose, coal tar and asphalt composition paints are used. Crude tar, heated to expel its moisture, and treated with lime and cement to neutralize its acidity, is reduced with light oils and benzol, thus forming quick drying paints suitable for many of the purposes mentioned. Utah gilsonite (asphalt), dissolved in turpentine or fused with drying oils and reduced with thinners, form very high grade bituminous coatings, well suited for protecting iron and cement which is to be immersed in water or acid solutions. These coatings are also used as baking japans upon hardware and other forms of metal equipment. Heated masses of asphalt, blown petroleum oil, and rosin are sometimes used as a bath in which hot iron water carriers are immersed in order to provide the carriers with a thick heavy coating which may be subsequently baked to increase its toughness. Such coatings are extremely resistant to moisture.

Marine Paints. When the bottoms of ships become fouled with attached animalculæ and marine growths, their speed is retarded to a great extent. The decay of timbers and the pitting of iron plates caused by such growths, are serious in many instances. Such conditions have made necessary the use of paints which would tend to keep the ships' bottoms clean and less subject to attack by marine organisms. Copper salts, on account of their fungicidal properties, were at one time added to boat paints. In other cases there was added small quantities of bichloride of mercury, ground in with the pigment. The water, however, would soon leach out the content of soluble mercuric salts The present practice is to provide a poisonous constituent in the form of mercuric oxide, a red

pigment which may be easily ground with the other pigments, and which in the presence of salt water gradually forms small percentages of the more poisonous bichloride, thus maintaining the "poison" efficiency of the paint over a longer period of time. Cyanide of copper is also useful as the toxic ingredient of bottom paints. Zinc oxide and iron oxide generally constitute the major part of such paints. As these paints are used below the water line they are made with a rapid drying varnish vehicle produced by dissolving shellac in alcohol. Pine tar oil and turpentine are also used in these paints to some extent. Upon iron vessels, previous to the application of the anti-fouling paint, there is generally applied a coat of anti-corrosive paint. The pigments used for this paint are generally zinc oxide, iron oxide, red lead, metallic zinc powder and zinc chromate. The pigments are mixed with shellac varnish. After dry-docking, the bottoms of small ships are sometimes scraped, primed with anti-corrosive paint, finished with anti-fouling paint and placed back in the water within a period of twenty-four hours.

Floor Paints. Paints highly resistant to abrasion are required for application to verandahs, kitchen floors, and similar surfaces which are subject to constant wear. Such paints are made upon a zinc, lead and inert pigment base, the inert pigment being either barytes or silica—pigments which are very resistant to abrasion. The pigment base is generally ground to a paste in linseed oil, and then mixed with a durable kauri gum mixing varnish and thinned with turpentine. When applied to wooden floors, these paints dry to a very glossy surface which becomes hard and extremely resistant to wear.

Water Paints. Whitewash was formerly one of the most widely used of cold water paints. There are many different formulas for the production of whitewash, the usual process being to mix slaked lime or whiting with a solution of glue. Casein is sometimes added to increase the binding properties, and Portland cement and salt in small quantities have also been added for special purposes. Calcimine, a popular type of cold water paint, is widely used for interior wall work. Calcimines are prepared as dry powders from gypsum or whiting as the pigment base. They often contain a considerable percentage of zinc, lithopone, clay and silica, and are tinted with limeproof colors such as the mineral oxides, umber,ochre,etc. The pigments are mixed with glue and the finished product sold in a dry powdered form, ready for use after mixing with water. In place of glue, casein has been extensively used as a binder. Although cold water paints of various types are widely used on account of their low cost, they are not washable and do not form as durable films as oil paints.

Wood Stains. For treating interior woodwork in order to imitate mahogany, cherry and other expensive woods, there are widely used special forms of prepared wood stains. Pigment stains are prepared from natural earth colors such as sienna, umber and ochre, sometimes mixed with aniline colors. These pigments are ground in boiled linseed oil and

thinned with turpentine, gloss oil, benzine, and benzol. The application of such stains to wood, fills the pores, producing a smooth surface, and at the same time stains the wood to a natural color, making a highly desirable finish over which floor varnishes are usually applied to produce hard-wearing surfaces. By grinding the pigment base in a hard, quick drying varnish, combination varnish-pigment stains are produced which fill, stain and varnish wood in one operation. Transparent wood stains are produced by adding to alcoholic solutions of shellac, small quantities of aniline colors. Very durable mahogany stains, well suited for application to floors, may be produced in this manner. Water stains for various kinds of hardwood trim, that is to be wax finished, are also used to a considerable extent. These are in some cases made from water soluble aniline compounds. The most durable water stains are made, however, by dissolving in water such chemicals as bichromate of potash, sulphate of iron, copper sulphate, etc.

Shingle Stains. A wide demand for a rather transparent preservative stain for shingles has been brought about through the use of shingles to such a large extent on bungalows and suburban villas. These stains are usually made by adding a small quantity of color ground in linseed oil to a large proportion of coal tar creosote, an organic substance which has proved an excellent preservative for wood. The product thus obtained may be thinned with benzine or benzol and gloss oil or similar drier is generally added in order to accelerate the drying of the product. Shingles dipped or brushed with such stains present a very pleasing appearance and give excellent service for years. For shingle roofs there is coming into wide vogue the use of oil paints containing a very high percentage of mineral pigments which are not reducible or affected by heat. When such paints are applied to shingled roofs, a coating quite resistant to fire is produced. The high percentage of mineral pigment present in the coating protects the wood from the effect of flying cinders or sparks.

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CHAPTER XVII

THE METALLURGY OF IRON AND STEEL

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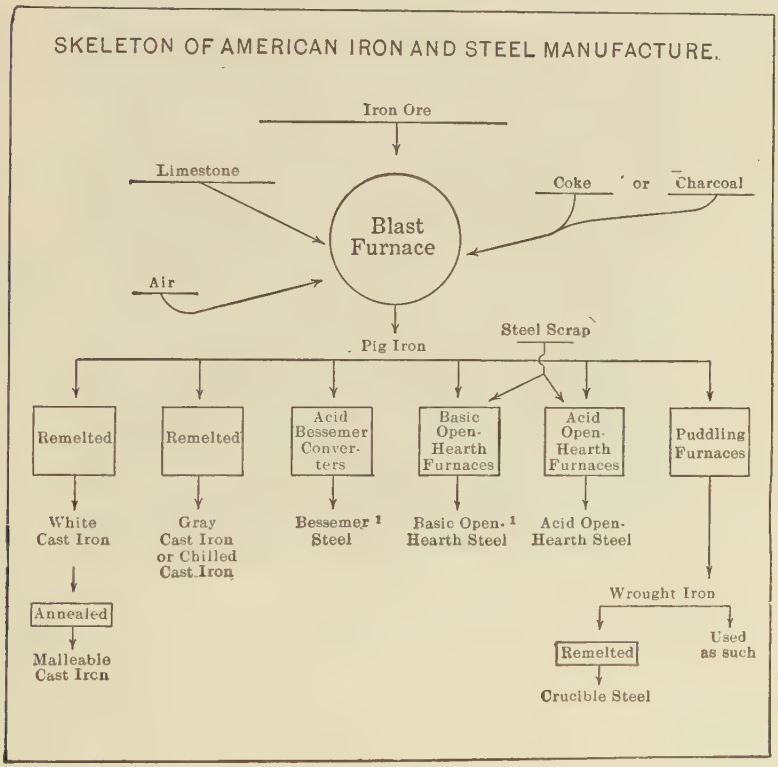
IRON is a metal and one of the commonest of the chemical elements on the earth's surface. From the magnetism of the earth we may also



infer that its interior is probably an iron ball, and that the supply is limitless provided we can get at it. The most important chemical properties of iron from a practical standpoint are: First, its liability to oxidation in damp air (i.e., rusting); second, the ease with which its oxides (ores) are

[1] A Duplex process involves the use of the basic open hearth preceded by the Bessemer process. Another Duplex process involves the super-refining of Bessemer or basic open-hearth steel in an electric furnace.

reduced at all temperatures above 500° F. (260° C.), and third, its very powerful chemical affinity for carbon.

Its most important physical properties are its strength, magnetism, and ability to become hardened and to retain a durable cutting edge after appropriate manufacture and treatment. In these three properties it can be made to excel all other known substances. Add to them its cheapness, and we can understand the importance of the ferrous metals to industry and to civilization. Another characteristic of iron which is of almost equal importance is its very unusual adaptability. To illus-

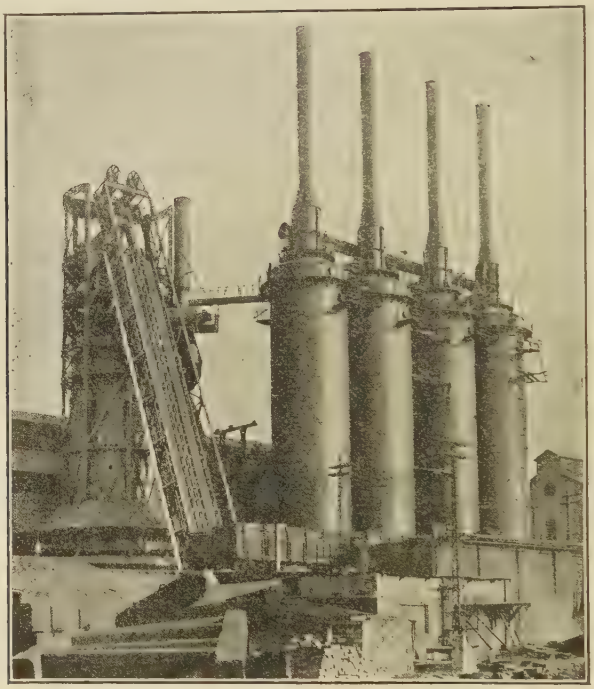


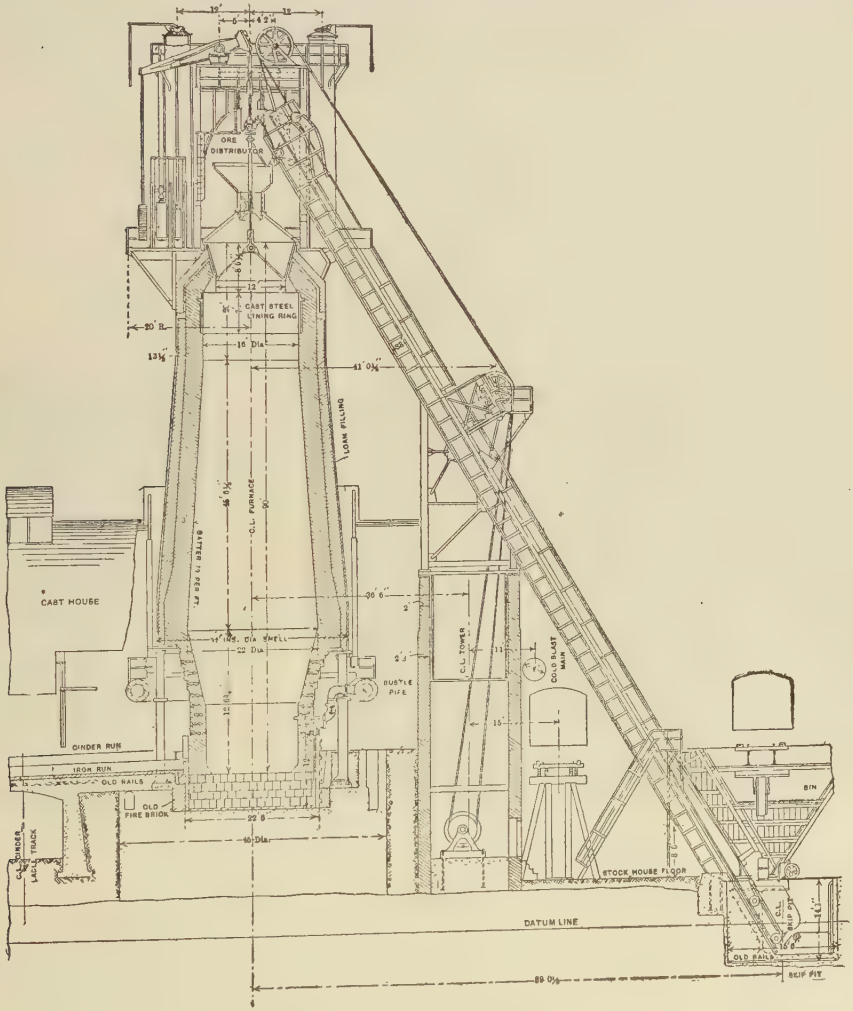
Fig. 184.—Blast Furnace and its Hot Blast Stoves.

trate this briefly: Iron can be made either the strongest or one of the weakest of metals; either the most magnetic or one of the non-magnetic metals; one of the hardest or one of the softest; one of the toughest or one of the most brittle; it may have a coefficient of expansion with changes in atmospheric temperature varying from almost zero to a maximum, and it may be given a combination of some of these different properties at will, according to the purpose for which it is to be fitted in service. And most of these variations are brought about by changing the amount of foreign elements by less than 5 per cent of the mass, or by giving it a different heat treatment, or by both together.

Ores. The chief ores are the oxides, Fe_2O_3 and Fe_3O_4. In only a few localities is the carbonate important. Unless the proportion of

iron is at least 35 to 45 per cent, the ore can not be smelted with profit, except where the cost of mining plus mechanical concentration is low.

Blast Furnace. Over 95 per cent of all the iron ore treated goes into the blast furnace, where it is smelted with coke and preheated air,[1] and a relatively impure grade of metal, known as pig iron, is produced. The modern



Cross Section through Blast Furnace

FIG. 185.

American blast furnace conforms in a general way to the lines and dimensions of Figs. 185, 186. A column of coke fills the body of the furnace from the bottom of the hearth to the top of the bosh (see Fig. 187), and above this

[1] More rarely charcoal fuel and cold air are employed, and under certain conditions, a mixture of coke and anthracite, instead of coke alone.

are alternate layers of coke and iron ore, together with an appropriate flux, which is generally limestone.

The preheated air, at a temperature of usually 800 to 1600° F. (425 to 850° C.) and at a pressure of about 15 lbs. per square inch, enters through the tuyere pipes at the top of the hearth, combines with the fuel and creates a volume of intensely hot reducing gases, which pass up through the interstices of the charge, melting, heating and reducing the ore which it meets, and finally passing out at the throat of the

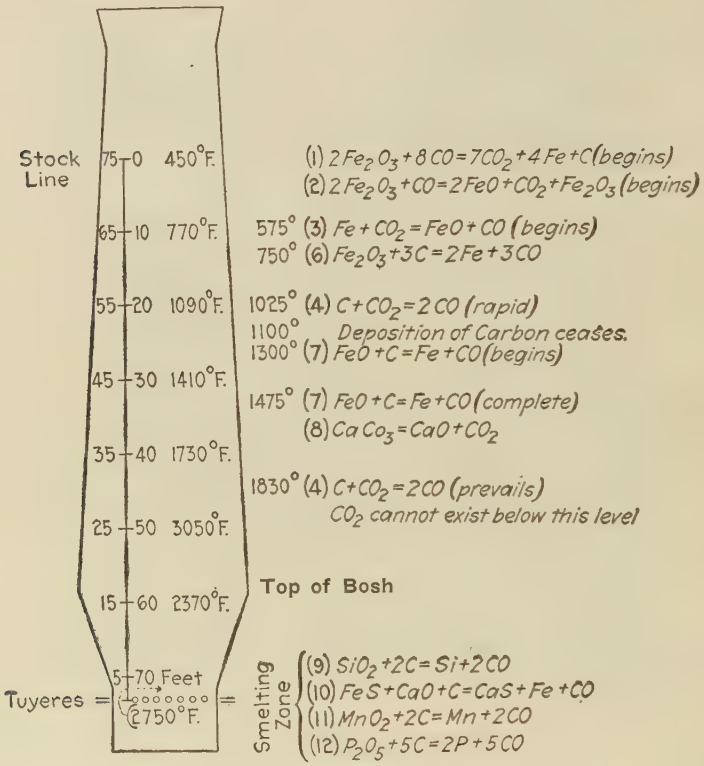


Fig. 186.

furnace. The temperatures at different points in the furnace and the various reactions which take place, are shown in a general way in Fig. 186. Below the top of the bosh the fuel is the only material not in liquid form. The iron, containing about 3.50 to 4.50 per cent of carbon and varying amounts of silicon, sulphur and other elements, according to the reactions of the smelting zone, collects in the bottom of the hearth, and on top of it the cinder, consisting of the impurities in the ore together with the ash of the coke and the lime, magnesia and impurities of the flux. All sulphur which is brought to the condition of CaS goes into the cinder, and all that in the form of FeS goes into the iron.

With this exception the cinder contains all the oxidized materials and the metal all those in reduced condition.

The cinder, because of its low specific gravity, floats on top of the metal and is drawn off about 15 times in twenty-four hours and disposed off. The metal is tapped out of the bottom of the furnace about every six hours and is either cast in the form of pigs or transported to a nearby steel mill in the liquid form.

The gas received at the throat contains about 22 to 27 per cent of CO and has a calorific power of 85 to 95 B.T.U. per cubic foot. About one-third of it is used for heating the four hot blast stoves which preheat the air used for smelting, and the remaining two-thirds is consumed under boilers or in gas engines, for the generation of power.

Because of its impurity and therefore its friability, pig iron cannot be worked or wrought. Many millions of tons per year are used in the form of iron castings, and the remainder purified. The purification consists in oxidizing the carbon, silicon, and some other impurities.

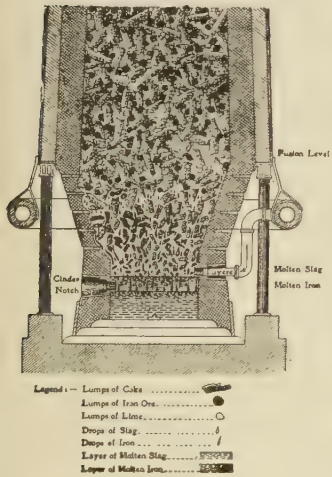


FIG. 187.

FIG. 188.

Manufacture of Wrought Iron. In the puddling process, Fig. 188, the impurities are oxidized by melting pig iron on a bed of iron ore. The ore gives up its oxygen to the impurities and some iron is reduced from it.

$$Fe_2O_3+3C=3CO+2Fe$$
$$2Fe_2O_3+3Si=3SiO_2+4Fe$$
$$5Fe_2O_3+6P=3P_2O_5+10Fe$$

At the end of about one hour and a half the carbon, silicon and manganese are almost entirely eliminated, as well as a portion of the phosphorus and sulphur. The iron is then drawn from the furnace in a pasty state, because the heat is not sufficient to maintain it in the liquid form

in a purified condition.[1] Wrought iron so produced is one of the purest of the iron and steel products. Its distinguishing characteristic is the webs and strings of slag mixed with it, which are drawn out by the rolling process, and give the metal its fibrous structure.

Crucible Steel. On account of its freedom from carbon, wrought iron lacks great strength and cannot be made to take a temper. If it be melted in crucibles with charcoal, pig iron, or some other substance rich in carbon, so that the resulting metal will contain from 0.75 to 1.50 per cent carbon, it makes a steel which is largely used for cutting tools and similar purposes, and is the highest in quality and price.

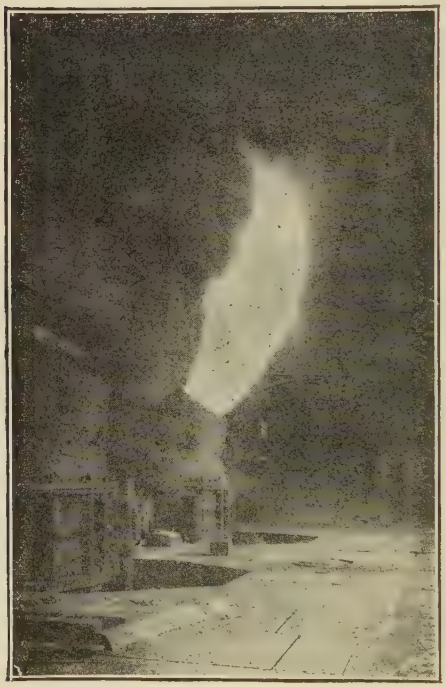


FIG. 189.—A Bessemer Blow.

Bessemer Steel. Pig iron is also purified by the Bessemer process, Figs. 189 and 190, in which cold air is blown through a bath of liquid pig iron. The oxygen of the air oxidizes the silicon, manganese and carbon and these oxidized materials separate in the form of a slag, with the exception of the latter, which passes off as gas (chiefly CO). The complete purification of 10 to 20 tons of liquid pig iron requires only seven to fifteen minutes of blowing. The heat produced by the oxidation of the impurities is sufficient not only to keep the bath in the liquid condition during the operation but also to raise its temperature more than 575° F. (300° C.). The liquid metal, however, dissolves a good deal of iron

TYPICAL ANALYSES IN THE HISTORY OF A BESSEMER BLOW

Minutes from Commencement of Blow.	Metal Bath.					Slag.					Escaping Gases.				
	C	Si	Mn	P	S	SiO_2	Al_2O_3	Iron Oxides.	MnO	Others.	CO	CO_2	O	N	H
Pig iron	4.00	1.00	0.50	0.090	0.070										
2	4.10	0.70	0.15	0.093	0.071	50.0	6.0	2.0	5.0	37.0	....	10.0	1.0	87.0	2.0
4	3.50	0.35	0.05	0.095	0.072	55.0	5.3	28.0	5.0	6.7	5.0	8.0	0.5	84.5	2.0
6	2.00	0.03	0.02	0.095	0.073	65.0	4.0	21.0	5.0	5.0	20.0	2.0	....	76.0	2.0
8	0.90	0.03	0.01	0.097	0.074	70.0	3.0	18.0	5.0	4.0	30.0	1.0	....	67.0	2.0
10	0.05	0.02	0.01	0.098	0.075	67.0	2.5	23.0	4.0	3.5	....	....	....	....	....
After Recarburizing	0.55	0.10	0.90	0.100	0.070	65.0	2.3	17.0	14.7	1.0	....	....	....	....	....

[1] The purer the iron the higher the temperature at which it melts.

oxide, which has a very harmful effect upon its qualities, but is nearly all removed by the addition of manganese at the end of the "blow."

The appearance of the "converter" flame gives an index by which the operation may be followed and controlled. When the oxidation of impurities is completed, the flame shortens, or "drops," and the blowing is discontinued. Then is added a predetermined amount of manganese to remove absorbed oxygen; silicon to prevent gas bubbles or "blow-holes," and carbon to give the desired degree of strength or hardness, or both.

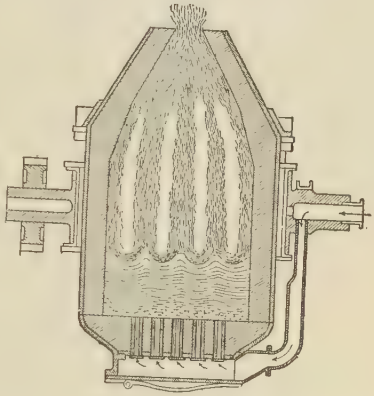


FIG. 190.—Section Bessemer.

Basic Bessemer. Acid Bessemer slags are rich in silica, and this prevents the elimination of phosphorus from the metal, because silica will force phosphorus out of the slag unless there is a great predominance of basic radicles present to unite with both silica and phosphoric acid. However, by using pig iron low in silicon, and also adding large quantities of lime to the bath in the converter, we may make a basic slag, which is retentive of phosphorus, and permits it to be removed after oxidizing, just as in the puddling process already mentioned. At the same time the lining of the converter is made of basic instead of acid materials lest it be attacked by the slag. The basic Bessemer process has not maintained a foothold in America because the supply of pig iron sufficiently rich in phosphorus has not been so abundant as to create the competition which produces low prices.[1]

Quality of Bessemer Steel. Bessemer steel is the lowest in price and poorest in quality, and in America this process is now rapidly giving way to the basic open hearth process, chiefly because the supply of ore from which to make pig iron suitable for the acid Bessemer process is yearly running lower. The great field of the Bessemer process has been in the manufacture of railroad rails, wire and pipe. For the two latter commodities it bids fair to retain its predominance for a time at least, because it is especially adapted to the manufacture of steel low in carbon.

Open Hearth Steel. The open hearth process depends upon Sir William Siemen's method of obtaining very high temperatures by the regenerative system. By this means a bath of iron may be maintained in a liquid condition at any degree of purity. The open hearth process really consists in remelting old steel scrap with varying amounts of pig iron. After the charge is melted, the impurities are oxidized by the

[1] Because the silicon in the basic pig iron must be low, the phosphorus must be high (1.75 per cent or more) in order to supply the necessary heat.

addition of iron oxide, usually in the form of ore or mill scale. It takes from three to four hours to melt and about an equal length of time to complete the purification.

Except in England, where a large amount of acid open hearth steel is made for ships, bridges and other structural purposes, the basic process is predominant. The basic furnaces are lined with magnesite or dolomite and the phosphorus as well as silicon, manganese and carbon, are oxidized to as low a point as may be desired. An important, although somewhat uncertain, amount of sulphur is also carried into the slag in the form of calcium sulphide, CaS.

Manganese and silicon must be added to the metal at the end of the open hearth process, as in the Bessemer process, but even under these conditions, basic open hearth steel is liable to contain dissolved oxide and also to be impregnated with gas bubbles or "blow-holes." For the best

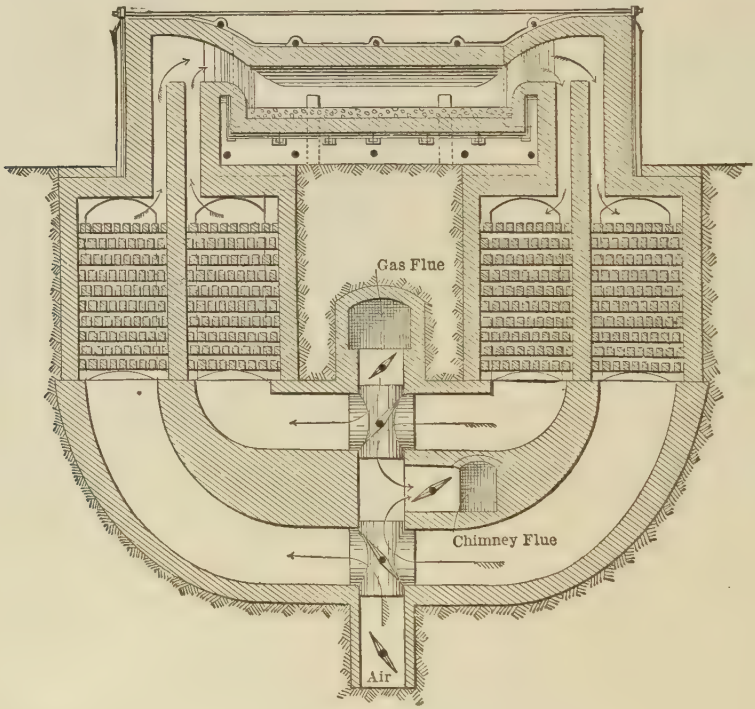


FIG. 191.

grades of structural steel and steel castings, the acid open hearth process therefore, maintains its importance, in spite of the higher cost of manufacture due to the price of low-phosphorous pig iron and steel scrap.

Duplex Process. The combination of the acid Bessemer and basic open hearth processes has recently become of much importance, because

it enables us to get some of the rapidity of working which is characteristic of the Bessemer purification, together with the elimination of phosphorus. The metal is usually first blown in a Bessemer converter until the silicon and manganese, and about one-half of the carbon, are eliminated, after which it is transferred, still in the liquid form, to the open hearth furnace where the remainder of the carbon and the phosphorus are oxidized.

Electric Iron and Steel. Electricity may be used as a source of heat in the smelting of either iron or steel, and in localities remote from fuel supply and adjacent to other cheap sources of power, experiments of this nature have been made with commercial success. They have excited a great deal of interest, although the volume of production has not yet attained relative importance. It is believed, however, that electric melting will give a cheaper, and a higher grade of steel than the crucible process, and important developments in this field have already begun. Electric furnaces are also the only means of producing some of the "ferro-alloys" because sufficient temperature cannot be otherwise obtained.

By means of electricity, temperatures may be obtained, hitherto unattainable with fuel, and an operation may be conducted in a non-

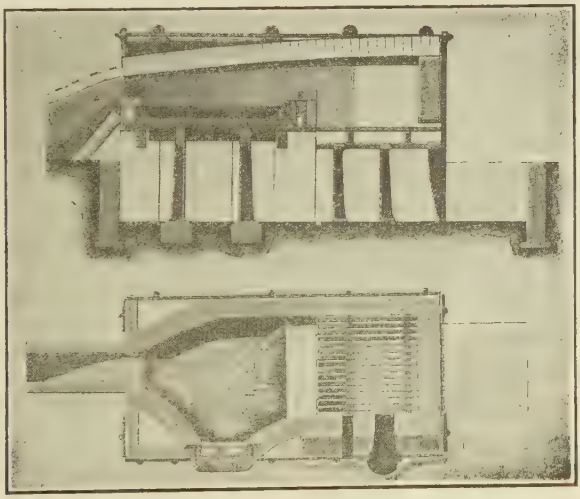


Fig. 192.

oxidising atmosphere. Therefore a duplex process, consisting of the purification of steel at a very high temperature in an electric furnace, subsequent to either the Bessemer or the open hearth operation, has resulted in a superior quality of steel (on account of freedom from dissolved gases and oxides, phosphorus and sulphur) at a medium cost.

Malleable Cast Iron. Iron castings lack strength and ductility on account of the impurities contained, and more especially on account of

the large flakes of graphite, which destroy the continuity of the metallic mass. On the other hand, steel castings are costly to make, not only because of the expense of purifying, but chiefly because of their relative infusibility and high shrinkage in cooling. A between-product has therefore been developed to which the name of " malleable cast iron " has been given, because, although its composition approaches that of ordinary

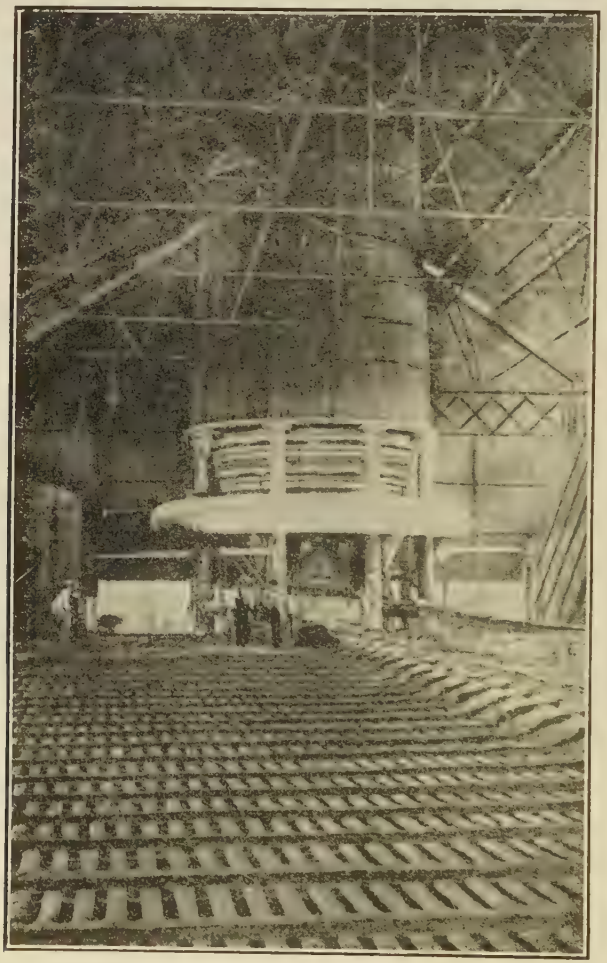


FIG. 193.—Pig Casting.

cast iron, it differs from it in having a limited amount of malleability. It also has greater strength than cast iron and a slight degree of ductility. Malleable cast iron is made by first making castings of white cast iron in which the carbon is usually under 3 per cent and all in the combined form. These castings are then maintained at a bright red heat for two or three days or more, which results in the carbon being precipitated in very minute flakes of graphite, known as " temper carbon." Temper carbon differs from graphite chiefly in the small size of its particles, and

the characteristics of malleable cast iron are due to this difference and also, in lesser degree, to the circumstance that the amount of carbon and phosphorus is less.

The Constitution of Iron and Steel. Iron and steel are not simple bodies but are of composite structure, formed of aggregations of different crystals. The nature of their constitution may be best understood by applying the modern theory of solutions. Space does not permit of our expounding this theory here, but those who have mastered it will understand its expression in the diagram shown in Fig. 194. The upper V-shaped curve of this diagram represents the freezing of the various alloys, or, as we sometimes express it, their crystallization from the liquid state. The upper left-hand freezing point locus, *AB*, represents the crystallization of iron containing about 2 per cent of carbon in solid solu-

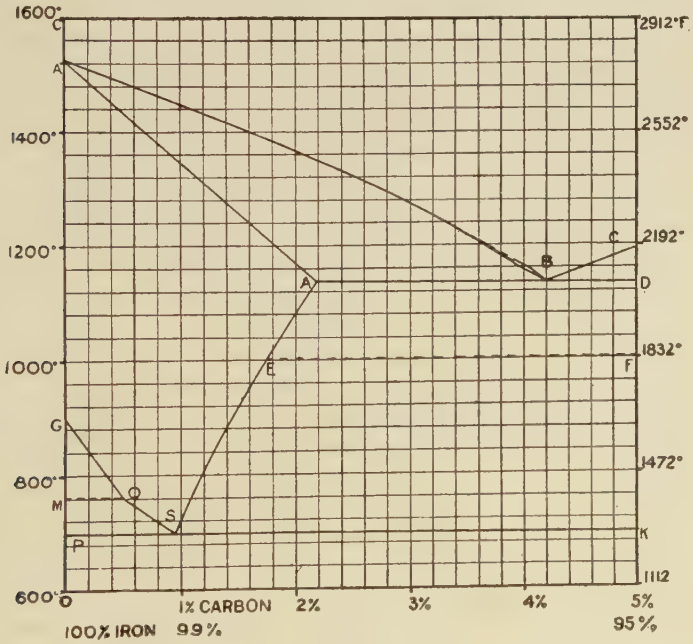


Fig. 194.

tion. The upper right-hand locus, *BC*, represents the crystallization of a compound known as cementite, having the chemical formula Fe_3C. The lower line, *aBD*, represents the freezing of the eutectic, which consists of a mixture of the solid solution before mentioned, and cementite. The ultimate analysis of this eutectic shows 95.7 per cent iron, 4.3 per cent carbon.[1]

[1] Those who have not mastered the modern theory of solutions should refer to Howe's "Iron, Steel and Other Alloys" and to later researches on Metallography given in the list of references.

The lower V-shaped curve represents the decomposition of the 2 per cent solid solution of iron and carbon previously referred to. The line *GOS* is the locus of the precipitation of pure iron (to whose crystals the name of ferrite is given). The line, *Sa*, is the locus of the precipitation of cementite, Fe_3C. The horizontal line *PSK*, is the locus of the formation of what Professor Howe has very aptly called the "eutectoid," consisting of 7 parts by weight of ferrite and 1 part by weight of cementite and showing on ultimate analysis about 0.85 per cent of carbon.

It is to be remarked that the ordinate extending through the point *a* is especially chosen as the boundary line between steel and cast iron. In other words, all the alloys to the left of the point *a* (that is to say, all those with less than 2.20 per cent carbon) are classified as steel, and all those to the right of this point are classified as cast iron. It will be noted that the foregoing paragraphs do not allow for the presence of graphite in cast iron. The occurrence of this metalloid has been the source of much research and discussion for which we have not space here. Suffice it to say that, in gray cast iron, the cementite which should be present according to the considerations mentioned above, is replaced in part (and sometimes in very large part) by graphite. This applies not only to the cementite theoretically born during solidification, but also that which is born in region *SaDK*, and during the formation of the eutectoid designated by ine *PSK*. The presence of silicon in cast iron is one of the strongest factors in promoting the presence of graphite instead of cementite. Rapid cooling from the liquid state on the other hand will tend to counteract this effect of silicon and produce an iron in which the carbon is in the form of cementite, or else is held in solid solution.

From the foregoing explanation we may observe that the iron alloys with less than 0.85 per cent carbon [1] consist of ferrite and the eutectoid.[2] The alloys between 0.85 per cent and 2.20 per cent carbon [3] will consist of pearlite and cementite. From these two classes graphite is not only theoretically absent, but in fact seldom occurs there. The alloys containing more than 2.20 per cent carbon include the whole class of cast irons, which will be termed "gray cast irons" if they contain 1 per cent or more of graphite, and "white cast irons" if their carbon is practically all in the form of cementite, or in the dissolved condition. When they contain but a fraction of a per cent of graphite, the cast irons will have a white surface on a freshly-broken fracture, with gray spots here and there, and to them is given the name of "mottled cast irons."

Properties of Ferrite. Ferrite is a weak, but very tough and ductile substance, having a high magnetic power and a relatively high conductivity for electricity as compared with the other constituents in iron and

[1] That is, wrought iron, soft steel, structural steel, machinery steel, railroad rails and even a great majority of spring steel.

[2] The name of "pearlite" is also given to the eutectoid.

[3] Comprising chiefly the steels used for cutting tools.

steel. We conceive that the weakness of ferrite is due in part to the large size in which its crystals ordinarily occur, and that this size is due in turn to their opportunity for growth, because they are born at a bright red heat in a relatively mobile mass. We come to this hypothesis because rapid cooling from just above the line *GOS* will not only decrease the size of the crystals of ferrite, but will greatly increase the strength of the iron.

Properties of Pearlite. The eutectoid is characterized by a very minute crystal size, so that high powers of the microscope are ordinarily necessary to discover its component crystals. This minute size is probably one of the reasons why steel with 0.90 per cent carbon has the greatest strength of all the normal slowly-cooled iron and steel alloys.

Properties of Cementite. Cementite is very brittle and hard, scratching glass with ease. It is magnetic but not nearly as strongly so as ferrite, and it is very fragile under shock. It is naturally of great service in cutting tools; but only within limits, because an excess renders the tool too fragile to bear the shocks of service. It is also useful for surfaces to resist abrasion, and on this account, the treads of cast iron freight car wheels, parts of rock-crushing machinery, etc., are locally chilled in order to rapidly cool them and produce white cast iron.

Properties of Austentite. Austentite is the solid solution of carbon in iron to which we have referred. The upper limit of carbon is about 2 per cent, although, by rapid cooling from the liquid state, and other abnormal means, we may greatly increase the amount of carbon retained in solution. The lower limit of carbon is, of course, zero. Austentite is hard, but not as much so as cementite, and it is also strong and brittle. As previously described in connection with the diagram, austentite has no normal occurrence in steel at atmospheric temperatures, but is completely decomposed into pearlite at about 1300° F. (700° C.), when the reactions on cooling are normal.

Properties of Graphite. Graphite is a soft substance, occurring in broad thin flakes which are themselves composed of thinner flakes, each having but slight adherence to the other. The chief effect of graphite in iron is to make it friable, weak and non-ductile. The weakening effect of the graphite is roughly in proportion to its amount, and also to the size of the individual flakes.

Effect of Combined Carbon on Iron. Combined carbon increases the strength of steel up to about 0.90 per cent, after which it has a weakening effect. It decreases the ductility, toughness, malleability, magnetic power and electric conductivity; increases the hardness both before and after quenching, and increases the brittleness.

Effect of Other Common Constituents. Manganese is added to steel for the purpose of removing dissolved oxide and also for neutralizing the harmful effect of the oxygen which it is not able to remove, as well as that of sulphur, because oxide and sulphide of manganese are not as harmful to iron and steel as the oxide or sulphide of iron. Sulphur

increases the "red-shortness" of iron and steel, i.e., their brittleness at a red heat and phosphorus increases the "cold-shortness," especially when the metal is subjected to shock. The upper limit of sulphur and phosphorus in steel should be 0.10 per cent and in high grades it is customary to specify that these elements shall be below 0.035 per cent. Silicon and aluminium are added to prevent the retention of gas bubbles or blow-holes in steel. Silicon is also added to cast iron in order to precipitate the carbon in the graphitic form, or to "soften" the metal as it is called. In this respect it is opposed by the action of sulphur which tends to produce white cast iron.

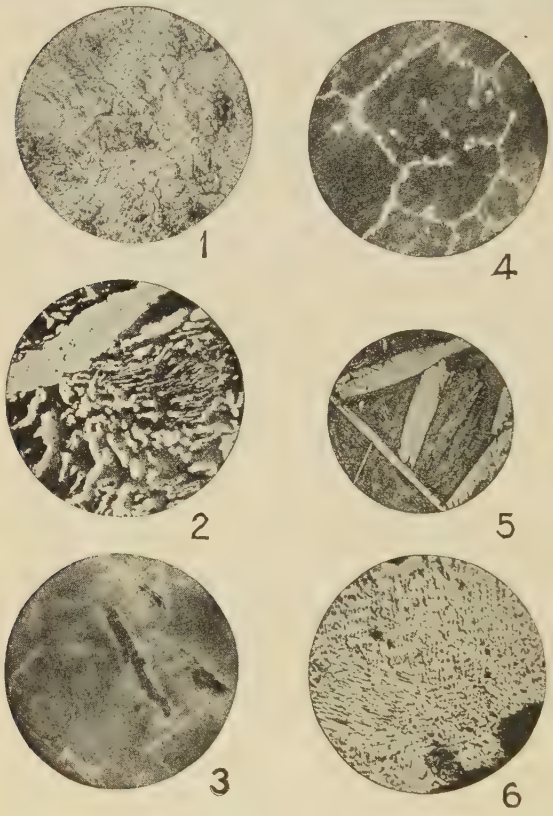


FIG. 195.

1. Electrolytic Iron; mostly Ferrite. 2. Steel of 1.50 per cent Carbon-Cementite and Pearlite. 3. Bubbles of MnS in Steel. 4. Steel of 0.30 per cent Carbon-Ferrite and Pearlite. 5. Spiegeleisen $(MnFe)_3$, C and Pearlite. 6. Phosphorus Eutectic, Fe_3P, and Iron.

Titanium and Vanadium. Titanium is the newest element commonly added to iron and steel and it seems to have a powerful influence in removing the last trace of dissolved oxygen and nitrogen, as well as increasing the fluidity of entangled oxides and slag in steel castings and ingots which enables these impurities to separate more easily from the mass. Titanium has already proved very beneficial in its addition in proportions of a few tenths of a per cent to railroad rails, and appears to have a beneficial effect in chilled cast iron and cast iron generally. Vanadium also appears to have a powerful effect in removing dissolved oxygen and seems to confer great strength on steel when used in combination with nickel or chromium.

Nickel Steel. The addition of nickel to steel in amounts up to $3\frac{1}{2}$ per cent increases its strength and elastic limit without, at the same time, decreasing the ductility as much as would be the case if the additional

strength were obtained by increasing the carbon. Nickel also reduces the rusting of steel and the segregation, and increases the soundness. Nickel-steel with 42 per cent of nickel has proven invaluable for certain measuring instruments, surveyor's tapes, pendulums, etc., because it is practically without expansion or contraction with changes of atmospheric temperature. The alloy with 37 per cent nickel has the same contraction and expansion with atmospheric temperature changes as has platinum and glass.

Manganese Steel. Steel with 12 to 15 per cent of manganese and in the neighborhood of 2 per cent of carbon is very resistant to wear and so hard and tough that it has proved very advantageous for railroad rails on curves, parts of rock-crushing machinery, burglar-proof safes, smaller sizes of armor-plate, etc. This material is very brittle when slowly cooled but, on heating to nearly a white heat and plunging into water, it becomes tough and ductile, thus reversing the ordinary effects.

Chromium Steel. Chromium is added to steel in amounts not more than 1½ to 2 per cent for the purpose of intensifying the hardness produced by heat treatment. It is very useful for such purposes as armor-plate, armor-piercing projectiles, parts of crushing machinery, etc. The combination of chromium with nickel, or with vanadium, together with special methods of heat treatment, such as double quenching, oil treatment, etc., produces a chromium steel with enormously high tensile strength.

High Speed Steels. Tungsten or molybdenum, when added to steel in proper proportions, produces a material which so greatly increases the efficiency of cutting tools as to have revolutionized machine shop practice and equipment. These steels are known as " high speed steels " because they do their cutting work so rapidly that the point of the tool may actually become a dull red through the heat of friction without losing its efficiency, and will last a longer time between grindings. The amount of tungsten in these steels is usually between 14 and 20 per cent, or else the amount of molybdenum will be between 6 and 12 per cent, while the carbon will be about 0.60 per cent.

Silicon Steel. Sir Robert Hadfield, the inventor of manganese steel, has also given us another alloy steel which has proven unusually efficient in magnets, because of its high permeability and high electric resistance. His patent covers the steel alloys containing 1 to 5 per cent of silicon, and the smallest possible amounts of carbon, manganese and other impurities. The steel is ready for use after a double (and sometimes a triple) heat treatment.

Heat Treatment of Steel. Under the " Constitution of Iron and Steel " we have mentioned that austentite, when slowly cooled, will break up into a conglomerate of pearlite, with either ferrite or cementite, this action taking place at about 700° C. (1292° F.). The chemical reaction is not an instantaneous operation, however, and may be prevented in part by

rapid cooling from above this temperature down to atmospheric temperature. Since austentite is much harder and stronger than its products of decomposition, the hardness of this treated steel may be controlled by the rate of cooling, such as quenching in ice water, warm water, light oils, heavy oils, etc., or else we may quench in water in the first instance and then " temper " the intense hardness thus produced by reheating the steel to temperatures varying between 220 and 330° C. (430 and 625° F.). At these low temperatures steel takes on a variety of colors due to the thin film of oxygen which forms, and it deepens from a light straw at 220° C., to a deep blue at 320° C. These are known as the temper colors.

Corrosion of Iron and Steel. The corrosion of iron is its greatest weakness from the industrial standpoint and involves a loss of millions of dollars each year. A great difference of opinion exists as to whether steel or wrought iron rusts the faster, but it is now generally understood that the difference between these two materials is not great, if both are well made. There is, however, a great superiority in well-made over badly-made material of either class. Steel which contains entrained slag, manganese oxide, iron oxide, much occluded gases or blow-holes, or in which the impurities are segregated, will yield more rapidly to rusting; and wrought iron, which contains an excessive amount of slag, not thoroughly worked, or which is irregular in composition, due to incomplete puddling or to the mixture with it of steel scrap during the welding process, or which has been made from low-grade scrap without remelting, will rust faster than well-made material. In short, it is now recognized that the quality of manufacture has a much greater effect than the process of manufacture. The old carbonic acid and hydrogen peroxide theories to explain the corrosion of iron, have now been replaced by the electrolytic theory, and it is recognized that any irregularity in the composition of the metal which produces a difference of potential, will hasten the rate of corrosion. There is also found to be a very great difference in the protective power of different paints and other coatings such as galvanizing, tinning, oxidizing, etc., for which the reader is referred to the recent treatise by Cushman and Gardner.

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CHAPTER XVIII

FERTILIZERS

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Historical. As far back as records go, the value of animal manures has been recognized in the growing of crops. Why they were of benefit and what relation their constituents bear to those of plants, are matters that have only been worked out during the past century. The earliest record of the use of mineral fertilizers is contained in a paper by Sir Kenelm Digby and printed in England in 1669. In this paper the use of saltpeter as a stimulant to plant growth is advocated. In 1804, Theo. de Saussure pointed out the significance of the ash of plants, and showed that without it plant life was impossible. Justus von Liebig in 1840 and 1842 was really the first practically to lay down the foundation of present fertilizer practice. By the middle of the nineteenth century the importance and value of nitrogen, phosphoric acid, and potash was pretty well known and it is from this time that the real growth, both of the use and knowledge of commercial fertilizers, dates.

Nitrogen as a fertilizer was first obtained from saltpeter and phosphoric acid was first derived from bones. Later nitrogen was obtained from by-products of slaughter houses and from ammonium sulphate, which is a by-product of coke-oven plants. Phosphoric acid was also obtained from petrified bone and from mineral phosphate beds in various parts of the world. The main source of potash at the present time is from the mines of Stassfurt, Germany.

Fertilizer Materials. Broadly speaking, there are two kinds of fertilizer materials: those which are in themselves a direct source of plant food, and those which, by their action, tend to make plant food fertilizers more available. While crops may grow without the use of fertilizers of the second class, no crops can mature without fertilizers of the first class.

Fertilizers of the second class comprise lime, gypsum, and common salt; they are all useful, but rarely indispensable. These are sometimes called "stimulant fertilizers." They tend to make rapidly available the stores of ammonia, phosphoric acid, and potash naturally present in the soil. When stimulant fertilizers are used exclusively for a term

of years, the soil loses ammonia, phosphoric acid, and potash. The inevitable result of such treatment must be finally the exhaustion of these important food constituents of the soil.

True fertilizers contain forms of plant food which contribute directly to the growth and substance of plants. Such materials may contain either ammonia, potash or phosphoric acid compounds, or all three.

Terms Used in Analysis. Fertilizer dealers and experiment station bulletins treat the different forms of fertilizer materials separately, and a familiar understanding of these trade names is important.

Ammonia is expressed either as nitrogen, as ammonia, or as nitrogen "equivalent to ammonia." There are various conditions in which phosphoric acid may be expressed such as reverted, available, insoluble, total, and phosphoric acid "equivalent to bone phosphate of lime." [1] Potash is expressed as potash, as potash actual, or as potash equivalent to sulphate of potassium or to chloride of potassium.

All genuine commercial fertilizers owe their value to the kind, quality, and amount of nitrogen, phosphoric acid, and potash they contain. They are made by mixing more or less of the several kinds of raw materials furnishing the desired ingredients, and to these may be added sulphuric acid to render the phosphoric acid available and a filler to make up the desired formula.

Nitrogen (Ammonia). Nitrogen is a gas, and in this form cannot be used in fertilizers; therefore, whenever we speak of nitrogen in fertilizers we do not mean that nitrogen exists in them as free nitrogen. The nitrogen in fertilizers is always combined with other elements and may be present in one or more different forms, such as nitrate of soda, sulphate of ammonia, or in the form of organic nitrogen as found in animal matter, such as blood, tankage, guano, or in vegetable matter, such as cotton-seed meal. Chemical analysis according to official methods does not really attempt to differentiate between the various forms other than to state whether or not the nitrogen in them is available. When, therefore, nitrogen is expressed in an analysis or guarantee as "ammonia" it refers to the entire amount of nitrogen present calculated as ammonia without regard to the form in which it is present. Ammonia consists of nitrogen combined with hydrogen and is also a gas and does not exist in fertilizers as such but in combination with other elements. Nitrogen equivalent to ammonia simply means that the total nitrogen content of the fertilizer is calculated to ammonia.

Phosphoric Acid. This as used in fertilizers does not exist as true phosphoric acid, but as various salts of phosphoric acid and lime. Soluble phosphoric acid is the mono-calcium phosphate formed during the process of acidulating phosphate rock or bone. Reverted phosphoric acid is the dicalcium phosphate which is also formed during the process of acidulation and is soluble in neutral ammonium citrate. Available phos-

[1] Phosphoric acid as used by the trade is not H_3PO_4, but the pentoxide (P_2O_5).

phoric acid is the sum of the soluble and reverted forms and is the total phosphoric acid in a condition capable of being absorbed by plants.

Insoluble phosphoric acid is the tricalcium phosphate as it exists in phosphate rock and bone and is not available for plant food. Total phosphoric acid is the total amount present irrespective of the form in which it is present. It is the sum of the above three forms. Phosphoric acid equivalent to bone phosphate simply means the total phosphoric acid calculated as the tricalcium phosphate.

Much research is being carried on in the endeavor to make bicalcic phosphate by other means than the addition of sulphuric acid to phosphate rock and several methods are now being tried out on a commercial scale, the phosphate being rendered soluble by means of heating in furnaces with various fluxes.

Phosphatic Crude Stock.

Furnishing insoluble phosphoric acid:	*Furnishing available phosphoric acid:*
Animal:	Animal:
Bones	Dissolved bone, acid-fish-scrap.
Mineral:	Mineral:
Apatite, phosphate rock from Florida, Tennessee, of blue, brown and white colors.	Acid-phosphate from any form of mineral phosphate.
Thomas Slag.	

Potash. This term as applied to fertilizers always means the oxide of potassium. It is not found as such in fertilizers, but as either chloride, sulphate, nitrate or carbonate of potassium, or as organic potash.

Potash soluble means the actual K_2O soluble in water and is the only kind considered in fertilizers.

Crude Stock Furnishing Potash. Muriate or chloride, kainit, containing both muriate and sulphate; sulphate; double manure salt; the double sulphate of potash and magnesia; less important salts are carnalite, krugite, sylvanite. Carbonate of potash, such as wood ashes. As organic potash, tobacco stems and ashes, cotton-seed meal. As nitrate, potassium nitrate.

Alunite, the hydrated sulphate of potash and alumina, is found in many places in the west and work is being done on it to determine its availability as a source of potash. It has been found that after ignition and leaching, over 90 per cent of the potash can be recovered as sulphate. It appears to be a very promising source for future supply of this material.

Geological Definitions. The primitive earths are four—clay, sand lime, and magnesia. Clay is called by geologists alumina, alumine, or argillaceous earth. Sand is called silex, silica, silicious earth or earth

of flints. Lime as it exists in the soil is commonly called calcareous earth. The term calcareous is not properly applied to any earth unless it will effervesce with acids. Each of these earths answers a determinate and specific purpose in the economy and growth of plants, and the perfection of soil lies in a mixture of the whole.

Bases of the soil are: the primitive earths which enter into its composition; vegetable matter: all vegetable substances in a decaying or rotten state; animal matter: all animal substances in a putrefying state; organic matter: a term applicable to both animal and vegetable substances in a putrefying condition.

Vegetable mould: the earthy remains of vegetable substances which have either grown and decayed in the soil or have been conveyed thither in the progress of cultivation.

Loam is a combination of vegetable mould with the primitive earths. *Marl* is a substance consisting of lime with a small portion of clay, and sometimes of peat with a marine sand and animal remains. It is useful as manure, and is distinguished by shell clay and stone marl.

Expression of Formulæ. One often sees formulæ expressed in this manner, 4–8–2, or 3–6–4. It means that nitrogen comes first, phosphoric acid next, and potash third, hence the 4–8–2 indicates a fertilizer containing 4 per cent of nitrogen, 8 per cent of phosphoric acid, and 2 per cent potash. These figures multiplied by 20 give for each ton 80 lbs. nitrogen, 160 lbs. phosphoric acid and 40 lbs. potash.

Explanations of Market Quotations; how to Estimate the Value of Fertilizers. Phosphate rock, kainit, bone, fish-scrap, tankage, and some other articles are commonly quoted and *sold by the ton.* The seller usually has an analysis of his stock, and purchasers often control this by analysis at time of the purchase.

Acid phosphate is usually quoted at so much "per unit" of available, that is, soluble and reverted phosphoric acid. The meaning of the term unit is explained below. Tankage is usually sold with a quotation of so much "per unit of ammonia" and "per unit of bone phosphate." The amount of bone phosphate may be calculated by multiplying the amount of phosphoric acid by 2.1850. On the other hand, the amount of phosphoric acid is calculated from the bone phosphate by multiplying the latter by 0.4576.

Sulphate of ammonia, nitrate of soda, and the potash salts are quoted and *sold by the pound,* and generally their wholesale and retail prices do not differ materially.

Blood, azotin, and concentrated tankage are quoted at so much "per unit of ammonia." To reduce ammonia to nitrogen, multiply the per cent of ammonia by 0.8228; to make the reverse calculation multiply by 1.2154. A "unit of ammonia" is 1 per cent, or 20 lbs. per ton. To illustrate: if a lot of tankage has 7 per cent of nitrogen equivalent to 8.50 per cent ammonia, it is said to contain $8\frac{1}{2}$ units

of ammonia, and if quoted at \$2.25 per unit, a ton of it will cost $8\frac{1}{2}$ times \$2.25, or \$19.13.

Tankage and fish-scrap are sometimes sold at a price, based on analysis, with regard to both the nitrogen and phosphoric acid which the product in question contains. For example: Tankage, 9–20 quoted at \$2.49 and 10 cents per unit, means that a given lot of tankage contains somewhere in the neighborhood of 9 per cent ammonia and 20 per cent bone phosphate, and is offered at \$2.49 per unit of ammonia and 10 cents per unit of bone phosphate. A unit of ammonia, 20 lbs. is equivalent to (20 times 0.8228) 16.46 lbs. of nitrogen and is quoted at \$2.49. One pound of nitrogen, therefore, costs $\frac{2.49}{1.65}$ equal to 15.10 cents.

A unit of bone phosphate, 20 lbs., is equivalent to 20 times 0.4576 equal to 9.15 lbs. of phosphoric acid, and is quoted at 10 cents. One pound of phosphoric acid therefore costs $\frac{10}{9.15}$ equal to 1 cent.

Hence it appears that a tankage containing 9 per cent ammonia and 20 per cent of bone phosphate and quoted at \$2.49 and 10 cents per unit, costs for nitrogen 15.1 cents per lb. and for phosphoric acid 1 cent per lb.

The cost of such a tankage will be 9 units of ammonia at \$2.49 equal. to \$22.41 plus 20 units of bone phosphate at 10 cents per unit, or \$2.00 or \$24.41 per ton.

Soil. Soils are generally divided into three groups: clay, loamy, and sandy. These in turn are subdivided as their general characteristics approach each other, thus:

Clay	Heavy clay
	Medium clay
	Loamy clay
Loamy	Clay loam
	Loam
	Sandy loam
Sandy	Loamy sand
	Sand

There are also other distinct forms, such as limestone, peaty and gravelly soils, but those given above best serve to describe the general conditions of farming lands. It is needless to enter into the details of soil formation beyond the general statement that clay is derived from the silicates of eruptive rocks, while sand is formed from the silica of quartz. The former due to a chemical decomposition, the latter rather to a mechanical subdivision. These two extremes have the following general composition as regards fertilizer constituents.

	Clay Soil, Per cent.	Sandy Soil, Per cent.
Potash	1.20	0.17
Phosphoric acid	0.15	0.11
Silica	72.52	81.01
Alumina	9.70	2.01
Lime	2.53	0.42

The presence of vegetable matter mixed with the soil gives that composition known as loamy. This vegetable matter is largely humus, a material of undetermined composition, and the function of which is still a subject of contention. The gradation of soils from heavy clay to sand is chiefly marked, by the varying proportions of clay and sand. Using the given classification, the variation of the two leading principles is approximately as follows:

	Clay, Per Cent.	Sand, Per Cent.
Heavy clay	90	10
Medium clay	75	20
Loamy clay	65	35
Clay loam	55	45
Loam	40	60
Sandy loam	25	75
Loamy sand	15	85
Sand	5	95

Properties of Soils. Before considering a specific fertilizer, the agricultural value of these different soils must be reviewed. The general characteristics of a clay soil are fine texture and cohesion of the particles. It absorbs moisture from the air and draws it from the lower soil by capillary attraction, and retains water obstinately. If worked while wet it becomes hard and intractable. A sandy soil has little adhesion of particles, attracts little or no moisture from the air, and allows water to percolate through it readily, thus causing loss of fertilizing elements by leaching. It absorbs and retains heat well and is dry and warm, easily worked and will not bake. Its power of drawing moisture from below is about two-thirds that of clay. Soils intermediate between sand and clay take, in a modified way, the main features of both.

For purposes of agriculture the circulation of moisture in the soil and the temperature are of greatest importance. A soil having clay as its predominant constituent holds its water almost stationary, and when subjected to evaporation, through heat or drying winds, bakes badly. The soil water contains fine particles of clay in suspension and these are drawn to the surface and deposited by the evaporation of the water, thus forming an upper layer no longer porous. Evaporation

ceases. The soil moisture, only a few inches below the surface, remains quiescent, and the closely packed upper layer also excludes heat and gases, the soil becomes cold, and those chemical processes necessary for the preparation of plant food in an assimilable form cease.

The best known remedy is applications of lime which throw down the suspended clay in the form of small granules, thus opening the pores of the soil and enabling a free circulation of water and the admission and action of gases and sunlight. With sandy soils evaporation does not bake and the movement of the soil waters is accelerated, but there is danger of exhausting the supply as the power of capillary attraction in this case does not greatly exceed a depth of 20 inches. These soils give free play to the action of gases and sunlight and maintain a temperature favorable to vegetation. Excessive evaporation is prevented by thorough tilling; a surface layer of finely pulverized earth a few inches deep arrests evaporation while it still maintains a fair degree of soil porosity and consequently the admission of gases and sunlight is not retarded. The action of chemical fertilizer is more prompt with sandy than with clay soils. Sandy soils however must be kept at work so to speak. They lose fertilizer elements rapidly through leaching if not protected by vegetation. As to temperature, a dark-colored soil, other conditions being equal, is usually warmer than one of lighter color; a soil having its percentage of sand high will rise in temperature slowly but will retain the heat longer than either loam or a clay soil; a wet (clay) soil is uniformly a cold soil.

Function of Soil Moisture. Evaporation of soil moisture cools the soil as the heat necessary to vaporize the water is drawn from the land. Evaporation, however, draws the moisture from below for very considerable depths and the fertilizing matters suspended or in solution are brought by this process within reach of the roots. To quote from the Wisconsin experiments: "Soil water is constantly in motion. When rain falls the moisture sinks into the soil carrying along with it oxygen, carbonic acid, nitric acid, ammonia, etc., and rendering plant food available, a part of which may be lost in the drainage if the rainfall is excessive. When the rainfall ceases evaporation commences and the soil water begins to rise carrying along with it dissolved plant food which accumulates in the surface soil. This power which soils have of drawing up water from their lower depths is known as capillary attraction and may extend down 6 or 7 feet."

Some idea of the immense amount of soil water thus brought to the surface may be gained from the fact that with the average soil, clay loam under cultivation, 660 lbs. of water per square foot is evaporated yearly, that is, 28,750,000 lbs. per acre. Computing from the average analysis of soil waters, this quantity of evaporation would bring to the surface soil about 14 lbs. of ammonia and 57 lbs. of potash; the phosphoric acid does not appreciably enter into soil solution.

It must be understood that these fertilizing elements are not gained, they keep constantly in circulation; at night they sink only to rise again when the evaporation commences with the succeeding sunrise. By this circulating system the fertilizing elements are brought within reach of the plant roots and are utilized; were it suspended, the application of manures would have to be increased many fold, as the quantity of the nutrients in the immediate vicinity of the plant itself would have to supply all its requirements; and as the roots of a plant in ordinary farming practice occupy probably less than 5 per cent of the total space, it follows that the efficiency of one ton of fertilizer, as at present, would require an application of 20 tons to accomplish the same results with suspended circulation of soil waters. This is why commercial fertilizers contain a disproportionate quantity of phosphoric acid as compared with potash and ammonia; the phosphates, to a great extent, take immediately in the soil an insoluble form and are rendered available as plant food only by the actual contact of the plant root hairs.

Action of Carbonic Acid on Soils and Rocks. All fertile soils contain a considerable amount of organic matter, and the presence of oxygen is necessary to accomplish its decomposition. Soils also contain innumerable bacteria, a part of which at least, are intimately concerned in the decay of organic matter and cannot live without oxygen.

One class of these bacteria decompose part of the soil's organic matter with the formation of carbonic acid gas. Water dissolves its own volume of carbonic acid gas under ordinary pressure, forming a solution of carbonic acid, $CO_2+H_2O=H_2CO_3$. With increased pressure a much greater amount is dissolved. When water is so charged it has a high solvent power for the carbonates of lime and magnesia, protoxide of iron and manganese. These salts are nearly insoluble in pure water. In this way carbonic acid plays a part of great importance in the growth of plants, since it enables water to convey to plants many fertilizing substances which are otherwise hardly available.

It is interesting to note here that the leaves of plants are white, in the absence of iron, and not green. By means of the microscope, the chlorophyl grains have been seen to grow and continue to prosper, as soon as a little iron was furnished to plants that had previously been without it.

The Liming of Land. Liming is likely to be profitable on the following classes of soils:

On heavy soils, particularly those through which surface water passes with great difficulty.

Soils of a lighter character if well stored with vegetable matter.

Newly graded or reclaimed land.

Old pastures where there is no white clover.

Peat and other sour soils that are invested with acid-loving plants.

Humus. Humus is a generic term applied to a group of closely allied substances, which collectively form the organic matter of soil. It cannot

be said that the precise chemical composition of humus is known, though a great deal of labor has been devoted by chemists to the study of the compounds, and several tolerably well defined chemical constituents are thought to have been isolated. The more clearly understood of these constituents are ulmin and ulmic acid, humin and humic acid, crenic acid, and apocrenic acid. Among the less known, the action of which is not yet understood, are xylic acid, saccharic acid and glucinic acid, besides a brown humus acid containing carbon, 65.8 per cent; hydrogen, 6.25 per cent; and a black humus acid containing carbon, 71.5 per cent; hydrogen, 5.8 per cent.

According to Mulder, the principal humus compounds are composed of carbon, hydrogen, and oxygen, in proportions as given in the following table:

Ulmin and Ulmic acid

Carbon.....67.10 per cent, corresponding to $C_{40}H_{28}O_{12}-H_2O$
Hydrogen.... 4.20
Oxygen.....28.7

Humin and Humic Acid

Carbon.....64.4 per cent, corresponding to $C_{40}H_{24}O_{12}-3H_2O$
Hydrogen.... 4.30
Oxygen.....31.30

Apocrenic Acid

Carbon.....56.47 per cent, corresponding to $C_{24}H_{24}O_{12}-H_2O$
Hydrogen.... 2.75
Oxygen.....40.78

Crenic Acid

Carbon.....45.70 per cent, corresponding to $C_{24}H_{24}O_{12}-3H_2O$
Hydrogen.... 4.80
Oxygen.....49.50

Sulphur Requirements of Soils. The average amount of sulphur in soil 3 feet deep is 5085 pounds per acre; this amount would be used up in from 70 to 285 crops, figuring on minimum and maximum requirements of various crops. In neighborhood of cities the sulphur is replenished from the air, but not in country districts.

Materials Furnishing Nitrogen; Guano. On the coast of Peru lie the Chincha Islands. These islands and the mainland opposite are in the dry zone of Peru in which rain seldom falls. They are small, high and rocky, barren and uninviting; yet from them has come vast wealth. Guano to

the value of one thousand million dollars has been taken from the Chincha Islands. It is doubtful if there be another spot of equal size on the earth which has yielded so much wealth as these guano beds. These islands, however, are not the only source of Peruvian guano, as the Macabi, Guanape, the Lobos, Ballestas, and the Huanillos, as well as scores of small islands have also furnished large quantities.

The word guano is the Spanish rendering of the Peruvian word *huanu*, meaning excrement. There are many varieties of Peruvian guano having different fertilizing values due to their different chemical constituents, but they all are alike in their origin. Guano is mainly the excrement of marine birds mixed with the remains of the birds themselves and the fish they have brought to land. In some cases on the Chincha Islands the deposits are from 160 to 180 ft. thick. The lower strata of such deposits may be thousands of years old.

Nowhere else in the world are marine birds found in such vast quantities as along the west coast of South America from Panama south to Chile. The larger number of these birds have their roosts and breeding places on the Peruvian Islands, or on points of the mainland. Their presence in such vast numbers is due to the quantity of fish found along these coasts.

Cormorants, pelicans, sea gulls, marine crows, in floçks numbering hundreds of thousands may be seen in these regions, while the rainless climate preserves the guano deposited. There are hundreds of bird islands in other parts of the world but the excrement and remains of birds found thereon are not the same as Peruvian guano, although the deposits may possess value for fertilizing purposes. Even with the Peruvian guano, analysis shows great differences.

All excrements contain nitrogen in the form of urates and salts of ammonia, but these are to a large extent lost unless the manure is at once applied to the land and even then the nitrogen may be washed out before it can become available for the plant. When left exposed to a humid atmosphere or when rain is allowed to fall on it the nitrogen salts are quickly leached out. The Peruvian guano, in its natural state, never having been exposed to rain or dampness, has retained its nitrogenous properties and as it is rich in all three elements of plant food it is more valuable than other guanos.

Guano has been used in Peru for centuries. As early as 1806 it was used in England, and in 1824, fifty vessels loaded annually at Chincha. It was used in the United States as early as 1832. Baron Humboldt in 1804 was the first to make the article known to Europeans, its commercial importance there dating from 1844. As before stated, the Chincha Islands were the first exploited. Nine million tons were extracted in ten years. Other deposits were developed in 1870. The Ballesta, Macabi, and Guanape Islands yielded 1,500,000 tons. Next the Lobos Islands were worked as well as the enormous deposits of the Province of Tarapaca on the south coast of Peru.

In reviewing this subject, L'Engrais of Paris estimates that in forty years over 18,500,000 tons were taken from these localities or about 440,000 tons annually.

As the penguins and pelicans are very voracious each bird is capable of furnishing on an average, about 32 gms. of excrement per night. It is estimated that 100 kgms. of guano, containing 14 per cent of nitrogen and 10 per cent of phosphoric acid, require the consumption of 600 kgms. of fish containing 2.3 per cent nitrogen and 1.7 per cent phosphoric acid. An annual deposit of 40,000 tons is, therefore, the digestive product of 3,420,000 pelicans. It is reported that while the old beds have been considerably reduced there are layers 30 ft. thick which have not been touched and which are still forming.

The Caribbean deposits are much lower in nitrogen than the Peruvian, but they run very high in phosphoric acid. In these much of the nitrogen has been leached out by the action of rain. The deposits found on the islands of Sombrero, Navassa, Aruba, Curacoa, Orchillas, Roncador, and the Pedro and Morant keys are similar to those found on the Caribbean coast.

The following table shows analyses made by the author on various grades and kinds of guano:

	Ammonia.	Phosphoric Acid.	Bone Phosphate.
Navassa (first cargo, 1856)	None	31.75	69.31
Brazilian	None	27.82	60.73
White Mexican (1858)	None	25.88	56.60
Peruvian standard	10.20	12.14	26.50
Peruvian (Lobos)	5.60	14.95	32.64
Peruvian (Chincha)	12.70	17.80	38.85
Grand Caymans Islands	None	25.16	54.92
Mona Island	None	24.21	52.85
Aves Island	None	18.92	41.30
Cay Verde (light)	0.80	29.85	65.16
Cay Verde (dark)	0.50	29.90	65.27
Orchilla Islands (soft)	None	20.60	44.97
Booby Island	1.30	10.54	23.00
Oruba	None	34.65	75.64
Avalo	None	30.50	66.58

The guano is taken out by shovel and pick. As the coasts are rough and few harbors exist, loading of steamers can be done in calm weather only. The water is very deep and large steamers can anchor close to the shore so that most of the guano can be loaded directly into the steamer from the shore by means of cable trams. In some cases, it has to be taken to the steamer in boats.

Calcium This is a product derived by heating calcium carbide in an atmosphere of nitrogen. The reactions are intricate, but may be represented by the following equation: $CaC_2+N_2=CaCN_2+C$. The technical procedure is simple, but care must be taken in carrying out

the details. The nitrogen must be technically pure and the complete nitrification of the carbide, necessary to produce a high grade product, is dependent upon progressive and cumulative reactions, which once started may not be checked or diverted at any stage except at the cost of the quality of the final product.

The following is a typical raw cyanamid proximate:

Calcium carbide	0.51%
Calcium cyanamid	68.02
Calcium carbonate	0.35
Calcium oxide	12.39
Free carbon	13.79
Silicon carbide	1.17
Aluminum carbide	1.67
Iron carbide	1.53
Not determined	0.57
Total nitrogen	23.81%
Total calcium as CaO	60.65

When freshly made cyanamid is a rich black crystalline substance. Upon exposure to moist air the calcium oxide present hydrates, not only adding weight to the material, but also increasing its volume. It was at first stated that a loss of nitrogen occurred, but this is not true. While the characteristic odor of ammonia is noted, careful check tests taken at various times have failed to show appreciable loss of nitrogen. For commercial uses, this hydration of the free lime accompanied by increase in volume is undesirable.

Small quantities of carbides, phosphides, and sulphides are frequently present in raw cyanamid, which are undesirable for many of the uses of cyanamid and notably so for its use as a fertilizer. When applied to the soil these materials form, after decomposition, acetylene, phosphine, and sulphuretted hydrogen. All of these gases are distinctly poisonous to vegetation and particularly so to seedlets at or during the period of germination. When cyanamid was first distributed to experimental agriculturists, it frequently contained as much as 8 to 10 per cent of these substances. Consequently the records of experimental research show many instances of poisonous action which were naturally charged against the cyanamid itself.

To prepare adequately the raw cyanamid for incorporation into fertilizers several processes have been developed and much costly machinery designed. The object of such processes being simply to hydrate all the caustic lime and to dislodge and expel as a gas all the substances in the raw cyanamid which will produce acetylene, phosphine, and hydrogen sulphide.

The finished product sold under the name of Improved Cyanamid

has the following composition. (This product is complementary to the analysis of the raw cyanamid given above.)

Calcium cyanamid	29.26%
Calcium carbonate	0.21
Calcium nitrate	20.06
Calcium hydrate	28.78
Sodium cyanamid	10.38
Free carbon	7.89
Silica	1.03
Alumina	1.37
Ferric oxide	0.69
Not determined	0.33
Total nitrogen	17.01%
Total calcium (CaO)	34.73
Nitrate nitrogen	3.39
Cyanamid nitrogen	13.62

Some 20 per cent of the total ammonia in improved cyanamid is present as nitrate, the remaining 80 per cent being present as cyanamid.

The combined nitrogen of cyanamid does not exist as ammonia in the material as marketed, but as an amide. Thus instead of being combined with three hydrogen atoms it is joined to two. In the presence of acids or of water cyanamid nitrogen slowly changes to the ammonia form.

For comparison the following two equations are given as being typical of the change in ammonium sulphate and calcium cyanamid due to action of the soil.

$$(NH_4)_2SO_4+Ca(OH)_2=CaSO_4+2H_2O+2NH_3$$
$$CaCN_2+3H_2O=CaCO_3+2NH_3$$

These two reactions may be effected by acid or basic salts. The results are the same, however, and the final product by the action of simple soil agencies in both cases is ammonia. Consequently, as a fertilizer, cyanamid nitrogen must be classed as ammonia nitrogen. It is true that cyanamid may pass into solution in an acid soil as urea, thus:

$$CaCN_2+2H_2O=CaO+CO(NH_2)_2.$$

Urea, however, in dilute solutions, slowly changes to ammonia (unless combined with a strong acid), as follows:

$$CO(NH_2)_2+H_2O=CO_2+2NH_3.$$

The soil contains far more water than lime, in the form of a soluble compound, and lime must be in solution to displace ammonia from

sulphate of ammonia. Under ordinary soil conditions cyanamid nitrogen is quite as rapidly converted into ammoniacal solutions as is sulphate of ammonia.

Calcium cyanamid is moderately soluble in cold water or water at ordinary soil temperatures. Its availability as a fertilizer as technically determined, is about the same as that of sulphate of ammonia and much greater than that of dried blood. It is doubtful, however, if in its actual crop-making power, in an average of all soils and under all conditions, it is more valuable than dried blood, or less valuable than ammonium sulphate. Under working soil conditions, in actual crop-making operations, relative availability is probably of less moment than intelligent application and thorough husbandry.

The latest technical observation upon the use of cyanamid in agriculture is the report of Prof. Jacometti of the Agricultural Academy, Turin, Italy, as follows: "Both calcium cyanimid and Norge nitrate have a fertilizing value about equal to that of sulphate of ammonia and nitrate of soda."[1]

Aluminum Carbo-Nitride. The above material was first made on a small scale in 1911 and is of interest as a future source of Nitrogen. The compound containing approximately 48 per cent nitrogen. At present time has not been worked out on large scale.

The following table is given as showing the relative fertilizing worth of different forms of ammonia in production of sugar cane.

Cane.	Sugar Made, Relative Tons.	Ammonia, Cost per Ton of Sugar.	Ammonia, Worth per Unit.
Cyanimid	1.00	$2.61	$2.65
Nitrate of soda	0.73	3.22	1.94
Sulphate of ammonia	0.66	3.41	1.75
Tankage	0.73	3.93	1.93

Dry Fish Scrap. The menhaden (*Brevoortia tyrannus*) belongs to the family Clupeidæ and has many local names. On the Maine coast it is called pogy, bony fish, moss-bunker; in Massachusetts, hardhead bunker; in Delaware, bug fish, in addition to those already given; on the Virginia coast, old wife, cheboy, ellfish, bug fish, green tail, and bughead; in North Carolina, fat-back and yellow-tail shad.

When full grown the fish weighs from 10 ounces to $1\frac{1}{2}$ lbs. and measures from 12 to 15 ins. in length. They are found in immense schools on the American North Atlantic coast from the Bay of Fundy to the Mosquito Inlet, Florida. Its usual habitat is the bays and rivers, sometimes as far as the brackish water extends, and ocean-ward as far as to the Gulf Stream. On the approach of warm weather the schools begin

[1] From an article prepared for the *American Fertilizer* in the office of the Technologist of the American Cyanimid Co.

to appear and remain until cold weather. Approximately a temperature from 60 to 70° F. appears favorable. In the Chesapeake Bay the season extends from March and April to November and December. The New Jersey fishing season begins about May 1st and ends about the middle of November. The habit of the fish is to congregate in very large schools and then swim along close to the surface of the water, packed closely side by side and tier on tier. As many as 450,000 tons of these fish have been taken in a single season.

As soon as the fish appear, steam and sailing vessels start out from the numerous factories along the coast and remain in commission until the fish have disappeared in the fall. In the spring the northern factories send their steamers south and they follow the fish north. In the fall they follow them south again until they get beyond the point where it is economical to fish for them. The average steamers are of about 80 tons burden and usually about 90 ft. long; such a vessel will take a cargo of from 250,000 to 300,000 fish. The crew consists of about 17 men. Larger steamers are used by some of the factories and in such cases two seines are carried. These steamers will hold from 900,000 to 1,200,000 fish and have crews of 24 men.

When a school of fish is sighted, the steamer gets as close as possible without scaring the fish and then lowers the two seine boats of whale boat pattern. The seine is a net from 750 to 1800 ft. long and 75 to 150 ft. deep with the usual fitting of cork and sinkers, and so arranged that the bottom may be drawn together, thus making a purse in which the fish are held. The two boats, each carrying an equal amount of the net, start in opposite directions around the school and when they have met, start pulling in the purse string. When the bottom is closed the steamer comes up and the fish are scooped from the net by means of large scoops worked by a derrick on the steamer.

When a steamer has a load it returns to the factory, as the fish, if kept too long, soon turn soft and are then very difficult to handle.

On reaching the factory, the fish are unloaded by being shoveled into a traveling conveyor which takes them to a belt which carries them into the store shed. From here they are carried to a continuous steam cooker, where the oil cells are broken and the fish bodies broken up. This requires but a few minutes, when the fish are run into screw presses. On leaving the cookers they contain about 75 per cent of water. The screw presses can press the fish down to about 45 to 50 per cent of water. Most of the oil is here liberated.

The water and oil are run into large settling tanks and the oil which rises to the top is taken off.

The fish from the presses then go to direct-heat or steam heated cylindrical dryers. They are dropped into the hot end of the dryer where the flame from either soft coal or oil is pouring in. The water in the scrap prevents the burning of the fish as it immediately takes

up the heat. The scrap falls to the bottom of the dryer and is carried around as it revolves and showered down through the hot gases. On reaching the end of the dryer it is cool enough to handle and contains about 8 per cent water. It is now picked up by a traveling belt and run to the storehouse where it is bagged ready for shipment. Great care must be taken in the storeroom, on account of the combustible nature of this material, owing to the presence of the oil left in it. It heats very rapidly if left in large piles and must be cooled by turning over.

The capacity of a factory is usually calculated as the number of barrels per day of fish that it can handle. One barrel contains 300 fish. A large and well equipped factory will handle 700 barrels of fish per hour, turning same out as wet acid scrap, or if the dryer capacity is equal to the cooking and pressing capacity as dry scrap.

To produce one ton of dry scrap requires an average of 50 barrels of fish, while to make one ton of acid scrap (wet) requires 30 barrels of fish. In a good season about 3 gallons of oil per barrel of fish is recovered.

Wet Acid Scrap. Where the plant does not have enough dryer capacity to take care of the catch, the excess is made into wet acid scrap. The fish scrap from the presses is acidulated with from 60 to 80 lbs. 60° Bé. sulphuric acid to the ton of wet scrap. This converts some of the bone phosphate into the available form and at the same time preserves the scrap from decomposition. Good acid scrap that has not lain long in piles will analyze on 50 per cent water basis as high as 7.50 to 7.75 per cent ammonia.

In many small factories instead of screw presses, hydraulic presses are used and the wet scrap is dried in the open air on large wooden drying floors.

The scrap must be turned over frequently and this is done by the use of harrows drawn by a horse. It has then to be piled, left to heat to some extent, again spread and turned. If the scrap is wet by a storm, the process has to be repeated. Dry scrap will run about 10 per cent water and 10.50 to 11.50 per cent ammonia, and will still carry 8 to 12 per cent oil.

Bat Guano. Deposits of this material are not of very great extent, consequently its importance as a fertilizer is small. It is used in localities where it is found. It is of very variable composition and by many is not considered of much value. The price paid for the ammonia content is not on a par with other sources of ammonia.

Horn and Hoof Meal. The horn and hoofs not available for more valuable purposes are slightly cooked until they become friable and are then ground to a fine powder for use. They run from 4 to 6 per cent water and 15 to 17 per cent ammonia.

Hair Stock. Most long hair is used for other purposes than fertilizers, but large numbers of South American hides are imported for

making leather and the short hair from these hides after being removed by the sweating process in tanneries is utilized as a source of ammonia for fertilizer manufacture. The ammonia of the hair without treatment is not available for plant food, but during the process of making acid phosphate the hair is subjected to the hydrofluoric acid fumes given off when the phosphate rock is treated with sulphuric acid and becomes decomposed; the sulphuric acid then unites with it and forms ammonium sulphate, thus furnishing available ammonia.

Leather Scrap. This is treated the same as hair stock in most cases, though in some cases it is dried till it is brittle and then ground into "leather meal."

Many states have laws against the use of either hair or leather as fertilizers.

Cotton-seed Meal. The products obtained from the cotton seed are lint, oil, hulls, and meal. The meal only is used in the manufacture of fertilizers.

Cotton-seed meal is obtained by grinding the cake which is left when the oil is pressed out. Its chief uses are as a cattle food and as fertilizer. The meal damaged by over heating can be used only for fertilizer purposes.

The average amount of meal, hulls, lint, and oil per ton of seed is as follows:

Meal	713 lbs.
Oil	282 "
Lint	30 "
Hulls	975 "

Fertilizing Value of Cotton-seed Meal. The plant food in cotton-seed meal is chiefly nitrogen, so that its fertilizing value depends upon the quantity of nitrogen present. It contains, however, an appreciable amount of phosphoric acid and potash. The average of 204 analyses is as follows:

Nitrogen	6.79%
Phosphoric acid	2.88
Potash	1.77

The trade value for these constituents is variable but taken at, nitrogen, 13 cents, phosphoric acid, 7 cents, and potash, 6 cents, the value as per above analysis per ton would be:

Nitrogen	$17.65
Phosphoric acid	4.03
Potash	2.12

This gives a total value of $23.80 per ton of 2000 lbs.

In using cotton-seed meal as a fertilizer it must be borne in mind that it is essentially a nitrogen provider, hence if the soil requires phosphoric acid and potash as well as nitrogen, the meal should only be used in connection with some form of fertilizer furnishing these other materials.

While the hulls are not used as fertilizer, still it is of interest to note their analyses as follows:

Nitrogen	0.69%
Phosphoric acid	0.25
Potash	1.02

Taking same values as above this would give a value of $3.35 per ton.

In 1905, 3,308,930 tons of cotton seed were produced with a value of $51,309,175.

Other Meals Not Much Used. Castor pomace obtained after oil pressed from castor beans, grape or tartar pomace, the refuse argols from manufacture of cream of tartar, and flaxseed meal obtained from pressed flaxseed are not of much importance. They contain varying amounts of nitrogen, phosphoric acid, and potash.

Utilization of Tank Water and Press Water from Tankage. After meat scrap has been cooked in the rendering tanks, it is allowed to settle to the bottom. The water and grease rise to the top and the grease is drawn off. The tank water is then run into a storage vat together with the water pressed from the tankage. This storage tank is provided with heating coils in the bottom. The water is here heated to about 170° Fahr., at which temperature any further grease which rises is skimmed off. It is important to remove as much of the grease as possible as it will interfere with the further process of evaporation. Most of the evaporating is done in double and triple effect evaporators. Fig. 196. Working with a triple effect the tank water is drawn into the first effect in such a quantity that it covers the heating space. When the steam is turned on it brings the water into rapid circulation and it begins to throw off vapor, which is conducted into the tube space of the next effect. When the first effect is working under a vacuum of 5 to 10 ins. and under a steam pressure of about 2 to 5 lbs., the second effect boils under a vacuum of about 15 ins. The vapor which then arises from the second effect is conducted into the tube space of the third effect which boils under a vacuum of 26 ins. The vacuum pump attached to the evaporating plant is sucking directly on the third effect and condenses the vapor which is thrown off from this third effect.

The tank water is kept at the same level in all three effects and as it boils down it is drawn over from the second to the third and from the first to the second, and fresh water is run into the first effect. In some evaporators this feeding of the tank water is automatic, the valves being left open so as to allow the tank water to run slowly from one effect

to the next until the liquid in the third effect is so heavy that it is ready to be pumped out.

The density of this tank water (which after completion of evaporation is called "stick") is from 26 to 30° Bé. at the temperature of the evaporator. This "stick" is pumped up in a storage vat provided with agitators and from this vat it is either run to the dryers which are drying the tankage and thus mixed with it, or is mixed with chemicals such as green vitriol and dried on internally steam heated rotating drum dryers. In this latter condition after being dried it is called "concentrated tankage" and runs 15 to 17 per cent ammonia. The green vitriol is added to keep the material from absorbing moisture and reverting back to the sticky condition, as it is very hydroscopic. In present practice most of the "stick" is dried with the tankage, thus raising the per-

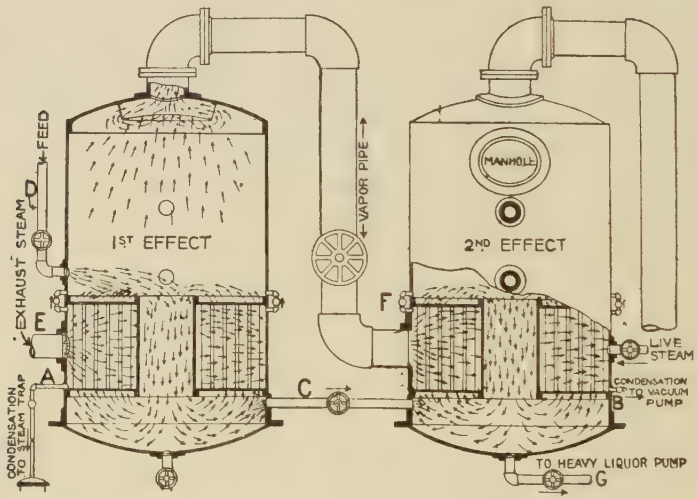

FIG. 196.—Evaporator. American By-Product Co., New York.

centage of ammonia in the tankage and doing away with the handling of a second product.

Slaughter House Tankage. In all slaughter houses the scrap meat is saved and treated for the production of "tankage." As all this material has more or less grease still adhering to it, it is first placed in large tanks and boiled under pressure till the grease has left the meat and the bone. The scrap is then allowed to drop to the bottom of the tank and the liquor is drawn off into large vats. After the grease has risen to the top it is withdrawn. The remaining liquor is then treated for its fertilizing constituents as given elsewhere under "concentrated tankage."

The scrap meat and bone, or as it is called "tankage" is now pressed to free it as much as possible from the water and adhering grease and is then dried in rotary direct-heat or steam dryers. It is then ready for sale.

In plants where the liquors are evaporated for "concentrated ankage" it is a general practice to mix the "stick" or thick liquor obtained by evaporation directly with the tankage before drying. This raises the percentage of ammonia and at the same time does away with the making of a second product.

There are several grades of tankage made, depending on the quantity of bone present. In small plants practically all the bone, except the very largest pieces, are left with the tankage. This gives a product running low in ammonia and high in bone phosphate. Such tankage may run from 5 to 8 per cent ammonia and up to 25 to 30 per cent bone phosphate.

In the larger plants, such as the Chicago packing plants, more care is taken to remove the bone, thus giving a tankage of higher ammonia content and lower bone phosphate. This will run about 11 per cent ammonia and 15 per cent bone phosphate.

There are three usual grades of tankage quoted in daily market reports as follows:

11 per cent ammonia and 15 per cent bone phosphate,
10 per cent ammonia and 20 per cent bone phosphate, and
9 per cent ammonia and 20 per cent bone phosphate.

The steaming, pressing, and drying do not remove all the grease. The best that can be done is to get it down to 6 to 8 per cent on the basis of the dried material, while frequently where factory practice is bad it will run as high as 20 per cent. This, of course, lowers the percentage of both ammonia and bone phosphate. As the grease balls the material and renders it hard to grind, its presence in large quantity leaves the tankage in bad condition for making into complete fertilizer. Where the fire hazard is not too great, and the plant is large enough, naphtha extraction is used to remove this grease from the dried tankage. Frequently in neighborhoods where a centrally located plant can obtain tankage from a number of small packing houses, naphtha extraction is employed, so that the grease and the grease-free tankage may be obtained. The grease is removed in these plants by subjecting the tankage to the solvent action of naphtha under pressure in large tanks holding from 10 to 20 tons of tankage. After a number of hours treatment, the temperature is reduced and the naphtha withdrawn. Live steam is then blown in to remove the excess of naphtha, the tankage finally withdrawn and spread over a large area to let the remaining naphtha evaporate. This process will remove all but 1 or 2 per cent grease.

Garbage Reduction.[1] The garbage is collected in wagons which have watertight steel bodies and sectional canvas covers. It is hauled to the central loading station and dumped into the garbage cars. The cars are constructed in semicircular bodies designed especially for handling garbage.

[1] Article by I. S. Osborn, engineer in charge of design and construction, Columbus, Ohio. Taken from *The American Fertilizer*.

The garbage when delivered is weighed on railway track scales and then run into the green garbage building, Fig. 197, on a siding which extends through it. The free water is drained off through a gutter extending the full length of the building. The swill water from the gutter is drained into a catch-basin, from which it is discharged into the grease separating tanks after which it is evaporated.

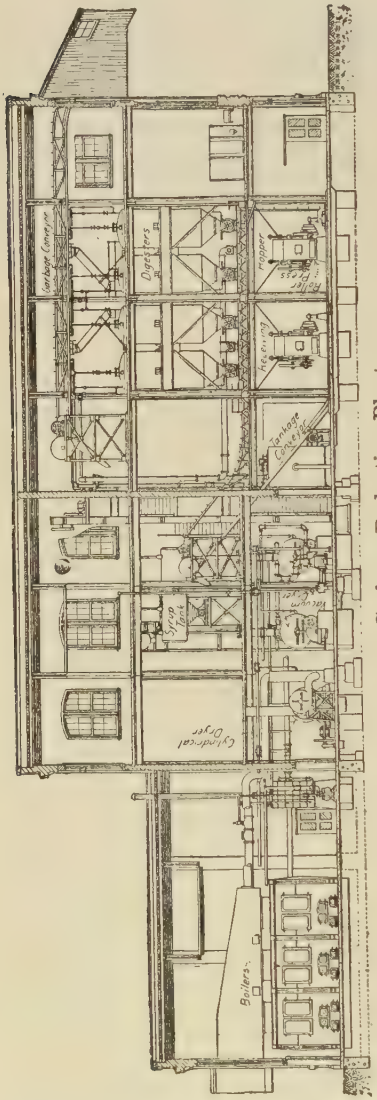

FIG. 197.—Garbage Reduction Plant.

The garbage is sorted and shoveled into a scraper conveyor, extending the full length of the building. This is a Jeffrey type conveyor and extends to the main building, carrying the garbage along the incline truss to the top of the main building and then along the bottom chord of the roof trusses and over the tops of the digesters. Connecting the conveyor with the digesters are swivel spouts which discharge the garbage directly into the digesters.

The digesters are 7 ft. in diameter by 14 ft. in length and have a capacity of 10 to 12 tons each. The inside is lined with cement and tile $1\frac{1}{2}$ ins. thick so as to protect the digester from wear, due to the agitating of the gritty matter when boiling, and at the same time to resist the action of the acids which would attack the metal. The digesters are arranged in nests of four and are connected with a common receiving hopper which is directly connected to the roller presses. The four digesters, one receiving hopper and a roller press are called one unit. The time required for cooking varies with the kind of garbage, but averages 6 hours with steam at 60 to 70 lbs. pressure as it enters the digesters.

The presses which are connected with the hopper are of the continuous roller type, especially designed by Charles Edgerton for handling garbage. They are directly connected to the bottom of the receiving hopper so that the material from the digesters passes through the presses without being exposed. The press is provided with an upper and lower conveying apron. The upper apron is made of $\frac{1}{2}$-in. steel slats riveted

to a heavy forged steel chain. The upper apron acts as the bottom of the receiving hopper, and when the press is running, carries the material through the feeding rolls and discharges it onto the lower apron. The lower apron is made of perforated slats $\frac{3}{8}$ in. in thickness and passes between six cast iron rolls arranged in pairs.

The pressed material is discharged at the front of the press into a Jeffrey scraper conveyor, which carries the material to the second floor of the drying department. The water and grease flow from the presses to catch-basins in the grease separating room. The grease is drawn off and pumped into storage tanks ready for shipment.

The liquor coming from the presses carries more or less solid matter in suspension. These solids are known as muck and silt. The muck settles to the bottom of the grease separating tanks and the silt rises to the top of the water. The tank water, after the grease has been separated, is drawn off to a large storage tank outside the building. The tank water contains 5 to 7 per cent of solids in solution; it is concentrated in a triple effect evaporator. After concentration the tank water is drawn off by a Magma pump and discharged into a storage tank on the second floor.

The muck and silt from the grease separating tanks are placed in a screw press from which the liquor flows to the catch-basins and the solids pass along the scraper conveyor to the dryer room. The solids are then fed to a revolving steam heated cylindrical dryer. The material is fed into the dryer continuously and discharged by means of two short spiral conveyors placed at the opposite end.

The dried material is then passed through the revolving screen. The screened tankage is then placed in the vacuum or mixing dryers, and the concentrated syrup added. The dry fibrous material acts as a filler and enables the moisture in the syrup to be driven off. The addition of the syrup to the fibrous material produces a higher grade of tankage from a mechanical and fertilizing standpoint.

The dryers are 15 ft. long and 5 ft. in diameter. Through the center of each dryer is a shaft to which paddles are attached for agitating and mixing the material. When dry, the material is discharged into another spiral conveyor connected to a Jeffrey bucket elevator, which discharges the tankage onto the third floor, where it is stored until shipped.

The Phosphate Rock Industry. From time to time various deposits of phosphate rock have been found and mined throughout the world, but the principal workings to-day are to be found in Florida, South Carolina, and Tennessee in the United States, in Algeria and Gafsa in North Africa, and in Ocean and Christmas islands in the far east.

The first serious attempt to obtain phosphate in this country was in Canada, mining what is known as Canadian apatite. This is a very high grade material, but it was very expensive to mine and when in 1870

the South Carolina, and in 1888 the Florida deposits were marketed, it could not compete with them. The rock in South Carolina is found in two grades—river and land pebble. It is deposited in considerable quantities along the margins of navigable streams and in the river beds between Charleston and Beaufort. The rock of Northern Africa, on account of its locality, is consumed entirely in Europe, and the production of the East Indies finds its market in Japan and Australia as well as in Europe.

Florida Phosphate. In 1889 pebble phosphate was discovered in De Soto County. Several months later land rock phosphate was uncovered at Dunellon in Marion County. This is the most valuable of the Florida phosphates and its discovery at once caused the investment of large amounts of capital. In the following year plate rock phosphate was discovered at Anthony in Marion County. Land rock phosphate is unlike the river and land pebble phosphate. The deposits in Florida are as a rule about 175 by 15 miles in area, parallel with the coast, and about 20 miles inland. Plate rock phosphate is mined only in a limited section of Marion County. It acts as a covering for limestone cones and is from 6 ins. to 1 ft. in thickness.

Pebble rock phosphate is almost entirely of marine formation and is located in the beds of small rivers and lakes and in areas originally covered with water. It is found far back from the coast in areas about 20 by 60 miles in extent and in tonnage produced surpasses both land and plate rock. Pebble rock occurs in the form of rounded pebbles varying up to a size somewhat smaller than a hen's egg. When a deposit is located it is first thoroughly prospected by boring with a core boring machine, as by this means the depth of the bed is ascertained as well as the grade of the various layers of phosphate encountered.

The mining is hydraulic. Powerful streams of water are thrown against the edge of the bed and the phosphate gravel together with the sand and clay is washed into a hole about 10 ft. in diameter and 10 to 15 ft. deep. The gravel is sucked up from this hole by means of a pipe and run to the mill which may be half a mile or more away. Here it is passed over screens which allow the fine silt and sand to escape while the phosphate pebbles are caught. This serves to wash the rock and it is then passed through direct-heat rotary dryers and carried by belts to the storage bins, ready for shipment.

As contracts are made for from 3 to 10 years shipments, it is very necessary that the property shall be thoroughly prospected, as it is necessary to know what grade rock can be obtained from different parts of the property. The prospecting is remarkably accurate. The actual factory returns usually show a yield agreeing within 1 per cent of what the prospecting had indicated.

Another method of mining this rock is by means of dredges which scoop the rock from the bottom of the river or lake and dump it into

cars which carry it to the mills. The extent of the bed of rock is ascertained by prospecting in a manner similar to the above until the area suitable for working is determined. The dredge is then brought up the river to the point where operations are to begin and starts digging into the side of the bank throwing the scooped up material into the cars. In some cases suction dredges are used and a partial separation of the rock and clay made on the dredge, the rock being dumped into cars and the sludge thrown out.

The bulk of the land pebble runs from 68 to 70 per cent *bone* phosphate, while high grade hard rock runs 76 to 78 per cent. The iron and alumina content is about 2 to 3 per cent.

Tennessee Brown Rock Phosphate. The Tennessee phosphates occur almost entirely in silurian and devonian strata, but more particularly in the former, and in the transition strata between the two. In December, 1893, blue rock phosphate was discovered in Hickman County. The beds of brown rock in this vicinity which are the finest phosphate deposits in the world, were not worked till later. Some 45,000,000 tons of this brown rock are estimated as being available for mining in this district. New fields are being continually opened up, railroads built and large quantities shipped. As the brown rock of this locality is gradually used, the vast blue rock fields of Maury, Hickman, and Lewis Counties will come into active development.

This brown rock lies in strata formation with layers of clay and earth as overburden. This overburden is stripped by hand or steam shovel and the soft wet phosphate taken out either by hand or steam shovel. It is carried to the washers where it is freed from the most of the clay and dirt. On account of the porous nature of this rock, the clay is disseminated all through it and it is very difficult to get rid of all the clay by the use of simple log washers. Many types of washers are used, the most efficient being the form used in cleansing glass-makers sand. This is done by pumping the fine material through pipes having sharp angles where the pressure is greatly increased. The clay is washed out in this manner and the clean rock is finally delivered to very deep settling tanks where the muddy water holding the clay in suspension is drawn off and the heavier rock which settles, after the tank is filled, is dried in rotary direct-heat dryers and is then ready for shipment.

This method is so efficient that a hand-car load of rock dumped through a space of 20 ft. will hardly raise any dust, whereas the rock cleaned by simpler and less efficient means will carry so much clay dust that a cloud of dust rises whenever it is disturbed.

Many of the smaller plants simply sun-dry the material, after it is dug, by spreading it on the fields and frequently turning with a harrow. When the rock is kiln-dried, large piles of wood are prepared about 10 ft. across and 20 to 40 ft. long and 5 to 6 ft. high. The wet rock is

piled on top and the wood fired. In case a storm comes up during the drying the whole operation has to be repeated, causing considerable expense.

Much of the material that is washed in log-washers or by use of revolving screens is more thoroughly cleansed of the adhering clay by blowing a very strong blast of air through the direct-heat dryers thus blowing off the lighter dust, or floats. This gives a fairly good material but the loss in phosphate is rather large as the floats will test from 50 to 60 per cent *bone* phosphate. It is very important to reduce the clay as much as possible as well as the iron and alumina phosphate, as these prevent the making of high available acid phosphate.

Tennessee Blue Rock. This rock is found in a territory bounded approximately by a trapezoid having at its four corners Centreville in Hickman County, Kinderhook and Mt. Joy in Maury County, and Lewis Monument in Lewis County. Traversing this territory are Duck River, Indian, Swan, Blue Buck, and Cathay's Creeks, and outcropping along these valleys and underlying the ridges between them are deposits of blue rock running in *bone* phosphate from 60 to 78 per cent, with less than 3 per cent iron and alumina oxides, that will aggregate nearly 40,000,000 tons.

Tennessee White Rock Phosphate. The deposits of white phosphate in Perry County, Tenn. have been formed by the deposition of phosphate from solution on the beds of limestone caverns. They are not of very great extent. Most of it is mined by means of open cut work although some tunneling is done. It lies in beds varying from a few inches to several feet in thickness.

Carefully selected specimens of the lamellar variety have run from 85 to 90 per cent of *bone* phosphate. The less dense, greenish material contains some ferrous iron and runs slightly less than 80 per cent.

South Carolina Phosphate Rock. This rock occurs in the form of nodules ranging in size from a pea to pieces the size of a man's head, and is found both upon the land and in the river beds. On the land the phosphate bearing strata are usually covered with sand to a depth of 6 to 10 ft., and vary from one to several feet in thickness. The mining on land is done by steam shovels which remove first the overburden and then the rock, which is screened, washed and dried. In the river beds a dredge is used to get out the rock which is then dried as usual. It runs from 50 to 60 per cent *bone* phosphate and about 6 per cent iron and alumina oxides.

The Western Deposits of Phosphate. As yet these deposits occurring in northern Utah, southeastern Idaho and southwestern Wyoming, while very large, are at present not developed, but they promise to be very large producers in the near future.

Phosphates in the South Seas. The islands of the Pacific Ocean contain the largest known deposits of high grade phosphates. The

deposits in Ocean and Pleasant Islands in the Gilbert group are estimated at 50,000,000 tons. About 300,000 tons yearly is being mined and shipped. About 100,000 tons is taken to Japan, 80,000 to Australia, and the remainder to Europe. Europe also receives yearly about 100,000 tons from Christmas Island. Recently good grade phosphate has been found on the islands in the French colony of Tahiti and dependencies. These islands, Makatea, Matahiva, and Niau, lie in the northwestern part of the Tuamotu Archipelago. The high grade deposits in Makatea are estimated at 10,000,000 tons with many million more tons of lower grade. These deposits range from 73 to 80 per cent *bone* phosphate content. It is estimated that when the works are completed and working at full capacity 200,000 tons yearly will be shipped. This island, together with the island of Angaur about 600 miles to the east of the Philippine island of Mindanao, is a coral island and has been for ages the resort of countless flocks of marine birds. Their excrement accumulated in vast quantities, but was not preserved unchanged as is the case in the guano islands. The heavy rains of this section of the Pacific caused a steady leaching of the soluble phosphates, which, coming in contact with the porous coral growth beneath of pure calcium carbonate gradually changed it into calcium phosphate.

Thomas or Belgian Slag. Thomas or basic slag is a by-product in the modern method of steel manufacture from ores containing noticeable quantities of phosphorus. The process of removing the phosphorus from the ore was first discovered by the English engineeers Gilchrist and Thomas and consists in adding to the converter containing the milled ore a definite quantity of freshly burnt lime, which, after powerful reaction, is found to be united with the phosphorus and swims on the top of the molten steel in the form of a slag.

The composition varies according to the character of the ore and the success of the process for removing the impurities. The following figures are typical:

Phosphoric acid	11–23%
Silicic acid	3–13
Calcium oxide	38–59
Ferrous and ferric oxides	6–25
Protoxide of manganese	1–6
Alumina	0.2–3.7
Magnesia	2–8
Sulphur	0.2–1.4

The fertilizing value of the slag was not recognized for a long time. A considerable portion of its phosphoric acid was found to be soluble in dilute citric and carbonic acids, which led to successful field experiments. The only preparation of the slag for fertilizer purposes when its value was first recognized, consisted in having it finely ground in

specially prepared mills so that 75 per cent would pass a sieve of 0.17 mm. mesh. This requirement was suggested by M. Fleischer, who used the slag with much success in improving marsh and meadow lands.

Previous to 1890, by means of pot, as well as by laboratory experiments, Wagner demonstrated that the phosphoric acid in different slags of the same degree of fineness, varied in its availability from 30 to 90 per cent, and further that many brands were adulterated with Belgian and other insoluble phosphates. The value is now determined by finding the percentage of phosphoric acid soluble in a 2 per cent citric acid solution, and these results are found to approximate very closely the results obtained by pot experiments.

The form in which the phosphoric acid exists in the slag has never been fully explained. It was formerly supposed that it was combined with lime as a tetracalcium phosphate and that this latter compound being less stable than tricalcium phosphate, under the influence of dilute acids became easily available to the plants by being decomposed into the calcium salt of the dissolving acid, and ticalcium phosphate. The tetracalcium phosphate, however, has never been made artificially, although it has been recognized under the microscope in the slag and exists as a mineral under the name of Isoklas.

More recent investigations have shown, as already indicated, that those slags of like phosphoric acid content which are richest in silicic acid give the best results. Hence the conclusion has been drawn that a part of the lime must be in the form of silicate. It is now generally held that the phosphoric acid is combined in the slag as a double salt of tricalcium phosphate and calcium silicate and that in this form the roots are able to utilize it. It is also believed that some of the phosphoric acid is more or less united with iron as a basic iron phosphate.

Bone. Bones consist of two distinct kinds of matter. One is mineral in character and consists of phosphate of lime or true bone phosphate; the other is organic, consisting of a flesh-like matter called ossein, which contains much nitrogen. An average analysis of bones is as follows:

Moisture	34.20%
Mineral matter (ash)	22.80
Fats	20.50
Albuminoids	20.60
Undetermined organic matter	1.90

The ash contained

Calcium phosphate	87.40%
Calcium carbonate	11.50
Undetermined mineral	1.10

Bones as a source of phosphoric acid for fertilizer manufacture come on the market in several forms. In large packing houses or in

localities where large amounts of bone can be collected, they are treated for the extraction of the gelatine, of which they contain about 33 per cent. To extract the gelatine the bones are steamed in tanks under 40 lbs. pressure for three or four hours. The gelatine being dissolved and the grease liberated, rises to the top. The grease is skimmed off and the liquor containing the gelatine drawn off for further treatment. The bones with some meat still adhering are removed from the tanks, dried and ground, producing "steamed bone meal." This contains from 4 to $4\frac{1}{2}$ per cent ammonia and 22 to 24 per cent bone phosphate. If steamed at a pressure of 50 to 60 lbs. and for a longer time, more of the gelatine is removed and the meal runs correspondingly lower in ammonia. Raw bone is bone that has been boiled in open kettles to remove the grease and gelatine; this method, however, is not so efficient as steaming under pressure and the bone meal runs higher in ammonia and lower in phosphoric acid.

Bone Black. For use in sugar refining, bones are calcined until black and brittle. This removes all the organic matter and renders them very porous. After their value to the sugar refiner is gone, they are sold to the fertilizer manufacturer as bone-black, containing about 30 to 35 per cent phosphoric acid and no ammonia.

Part of the phosphoric acid in steamed or raw bone meal is in the available form. This class of bone is a very good fertilizing material as the phosphoric acid is decomposible in the ground and in the course of four or five years is rendered all available, thus furnishing a steady supply of phosphoric acid to plant growth. The phosphoric acid of bone-black or bone ash is, however, entirely unavailable without treatment with acid. Superphosphate and dissolved bone-black are terms applied to the bone meal and bone-black which have been acidulated so that the phosphoric acid is rendered available for plant growth.

Chemistry of the Manufacture of Acid or Super-phosphate. The reaction which takes place on the addition of sulphuric acid to phosphate rock or bone is as follows:

$$3Ca_3(PO_4)_2+6H_2SO_4+12H_2O=4H_3PO_4+Ca_3(PO_4)_2+6CaSO_4\cdot 2H_2O$$

and

$$4H_3PO_4+Ca_3(PO_4)_2+3H_2O=3CaH_4(PO_4)_2\cdot H_2O$$

A simpler form of the reaction is expressed as follows:

$$Ca_3(PO_4)_2+2H_2SO_4+5H_2O=CaH_4(PO_4)_2\cdot H_2O+2CaSO_4\cdot 2H_2O.$$

If 310 parts by weight of finely ground tricalcic phosphate be mixed with 196 parts of sulphuric acid and 90 parts of water, and the resulting jelly is quickly diluted with water and filtered, there will be found in the filtrate about three-quarters of the total phosphoric acid as free acid.

If, however, the jelly at first formed as above, is left to become dry and hard, the filtrate, when the mass is beaten up with water and filtered, will contain monocalcic phosphate $CaHPO_4$.

If the quantity of sulphuric acid used is not sufficient for complete decomposition, the dicalcium salt is formed directly according to the following reaction:

$$Ca_3(PO_4)_2+H_2SO_4+6H_2O=Ca_2H_2(PO_4)_2\cdot 4H_2O+CaSO_4\cdot 2H_2O.$$

This arises doubtless by the formation at first of the regular monocalcim salt and the further reaction of this with the tricalcium compound as follows:

$$CaH_4(PO_4)_2+H_2O+Ca_3(PO_4)_2+7H_2O=2Ca_2H_2(PO_4)_2\cdot 4H_2O.$$

This reaction represents, theoretically, the so-called reversion of the phosphoric acid. When there is an excess of the sulphuric acid there is a complete decomposition of the calcium salts with the production of free phosphoric acid and gypsum. This reaction is represented as follows:

$$Ca_3(PO_4)_2+3H_2SO_4+6H_2O=2H_3PO_4+3(CaSO_4\cdot 2H_2O).$$

The crystallized gypsum absorbs the 6 molecules of water in its structure,

Reactions with Fluorides. Since calcium fluoride is present in nearly all mineral phosphates, the reactions of this compound must be taken into consideration in the chemistry of this subject. When treated with sulphuric acid the following reaction takes place:

$$CaF_2+H_2SO_4=2HF+CaSO_4.$$

The free HF then reacts with any silica present as follows:

$$4HF+SiO_2=2H_2O+SiF_4.$$

This compound, however, is decomposed at once in the presence of water, forming hydrofluosilicic acid, as follows:

$$3SiF_4+2H_2O=SiO_2+2H_2SiF_6.$$

The presence of fluorides is very objectionable both on account of the dangerous gases evolved during the manufacture and because 100 lbs. of calcium fluoride will consume 125.6 lbs. of the sulphuric acid.

Reaction with Carbonates. Most mineral phosphates contain carbonates in varying quantities. On treatment with sulphuric acid these are decomposed as follows:

$$CaCO_3+H_2SO_4=CaSO_4+H_2O+CO_2.$$

When present in only moderate quantities they are not objectionable as the reaction produces a rise in temeprature throughout the mass, and the CO_2 formed permeates and lightens the whole mass, assisting thus in completing the reaction by leaving the mass porous, and capable

of being easily dried and pulverized. When large quantities are present, however, additional water should be added to furnish the proper amount for the crystallization of the gypsum. 100 parts by weight of calcium carbonate require 125 parts of 60° Bé. acid.

Solution of the Iron and Alumina Compounds. Iron may occur in mineral phosphates in many forms. It probably is most frequently present as ferrous or ferric phosphate, seldom as oxide and often as pyrite. The alumina is chiefly present as phosphate and as silicate. When, as is generally the case, a little less sulphuric acid is employed than is necessary for complete solution, the iron phosphate is attacked as follows:

$$3FePO_4+3H_2SO_4=FePO_4\cdot 2H_3PO_4+Fe_2(SO_4)_3.$$

A part of the iron sulphate formed reacts with the acid calcium phosphate present to produce a permanent jelly-like compound, difficult to dry and handle. By careful practice as much as 4 to 6 per cent may be handled, but over 2 per cent is objectionable. Pyrite and silicate are not attacked by the sulphuric acid and these compounds are therefore not objectionable and no account is taken of them in analyzing phosphates.

With sufficient acid the alumina phosphate is decomposed with the formation of aluminum sulphate and free phosphoric acid, as follows:

$$AlPO_4+3H_2SO_4=Al_2(SO_4)_3+2H_3PO_4.$$

Reaction with Magnesium Compounds. The mineral phosphates, as a rule, contain but little magnesia. When present it is probably as an acid salt, $MgHPO_4$. Its decomposition takes place in slight deficiency or excess of sulphuric acid respectively as follows:

$$2MgHPO_4+H_2SO_4+2H_2O=[MgH_4(PO_4)_2\cdot 2H_2O]+MgSO_4.$$

and

$$MgHPO_4+H_2SO_4=H_3PO_4+MgSO_4$$

The magnesium, when present as oxide, is capable of producing a reversion of the monocalcic phosphate as follows:

$$CaH_4(PO_4)_2+MgO=CaMgH_2(PO_4)_2-H_2O.$$

One part by weight of magnesia can render $3\frac{1}{2}$ parts of soluble monocalcic phosphate insoluble.[1]

Wood and Lime Kiln Ashes. These are chiefly valuable as fertilizer materials on account of the potash they contain. A good grade of unleached wood ashes should contain about 5 to 6 per cent potash, while the lime kiln ashes will run slightly lower. They both contain about 2 per cent phosphoric acid.

Tobacco Stems and Dust. These contain ammonia, phosphoric acid, and potash, the latter being the highest. Stems will run 2 to 3

[1] From Prin. and Practices Agric. Analysis. H. W. Wiley.

per cent ammonia, and 7 to 8 per cent potash. The dust runs slightly higher in ammonia and from 2 to 3 per cent potash. Both carry small amounts of phosphoric acid. Tobacco dust is valuable as a filler on account of its absorbent properties.

Cotton-seed Meal Ashes. This material contains about 10 per cent total phosphoric acid, 8 per cent available phosphoric acid and 17 to 18 per cent potash.

Manganese Manures. Using 50 pounds of sulphate of manganese to the acre on oats increases yield 20 per cent. Rice 30 per cent and barley, wheat, corn, peas, beans, carrots, etc., in proportion. Should be applied in several doses and as top-dressing to get best results.

Night Soil. The material collecting in cesspools is pumped upon sandy soil, where it is allowed to dry. This is used locally and constitutes a valuable fertilizer.

How to Calculate Amounts of Material to be Used in Making a Complete Fertilizer of Definite Composition from the Raw Materials. Suppose that we desire to make a fertilizer having the composition: nitrogen 4 per cent, phosphoric acid 8 per cent, and potash 10 per cent. Suppose in addition that we have on hand the following materials: nitrate of soda containing 16 per cent nitrogen, acid phosphate containing 15 per cent available phosphoric acid, and muriate of potash containing 50 per cent actual potash (K_2O). How many pounds of each of these materials will we require?

To contain 4 per cent nitrogen, the ton must contain 80 lbs. Nitrate of soda contains 16 lbs. of nitrogen in every 100 of the nitrate, and hence 500 lbs. of nitrate of soda would be required to make up the 80 lbs.

To contain 8 per cent phosphoric acid, the ton must contain 160 lbs. The phosphate contains in every 100 lbs. 15 lbs. of phosphoric acid and hence 1067 lbs. of the acid phosphate will be required to furnish 160 lbs. available phosphoric acid.

To contain 10 per cent potash the ton must contain 200 lbs. Our muriate contains in every 100 lbs. 50 lbs. actual potash, and hence 400 lbs. will be required to give the 200 lbs.

We should then have the following:

500 lbs. nitrate of soda,
1067 lbs. acid phosphate,
400 lbs. muriate of potash,

or a total of 1967 lbs. Now to make it up to one ton we simply add 33 lbs. of any inert material such as dirt for instance, and we then obtain one ton of fertilizer of the desired composition. By adding one more ton of "filler" we should have two tons of fertilizer of the following composition: nitrogen, 2 per cent, phosphoric acid, 4 per cent, and potash, 5 per cent.

Now for a more complicated example suppose we wish to make a

fertilizer of the same composition, but instead of having three materials, each containing only one ingredient, suppose we have on hand Peruvian guano, containing 3 per cent nitrogen, 18 per cent phosphoric acid, and $3\frac{1}{2}$ per cent potash.

To give us 160 lbs. (8 per cent) of phosphoric acid we shall require about 900 lbs. of this guano. Nine hundred pounds would also supply 27 lbs. of nitrogen and 31 lbs. of potash. But we require 80 lbs. of nitrogen and 200 lbs. of potash in all, or 53 lbs. more nitrogen and 169 lbs. more potash to complete the mixture. Three hundred and eighty-four pounds of nitrate of potash analyzing 14 per cent nitrogen and 44 per cent potash would supply this 53 lbs. nitrogen and also the 169 lbs. potash, therefore we have

	Nitrogen.	Phos. Acid.	Potash.
900 lbs. guano containing	27 lbs.	160 lbs.	31 lbs.
and			
384 lbs. nitrate of potash	53 lbs.		169 lbs.
or total of			
1284 lbs. containing	80 lbs.	160 lbs.	200 lbs.

now by adding 716 lbs. of filler we have one ton of fertilizer of the desired formula.

For a third example, suppose we have the following materials:

1st. one containing 3 per cent nitrogen, 18 per cent phos. acid, and $3\frac{1}{2}$ per cent potash
2d. one containing 6 per cent nitrogen, 9 per cent phos. acid and 2 per cent potash
3d. one containing 50 per cent potash

we would then take

		Nitrogen.	Phos. Acid.	Potash.
1st.	300 lbs. containing	9 lbs.	54 lbs.	10 lbs.
2d.	1200 lbs. containing	72 lbs.	108 lbs.	24 lbs.
3d.	332 lbs. containing			166 lbs.
Total	1832	81	162	200

By adding 168 lbs. of filler we then have one ton of our fertilizer.

A filler in common use is obtained from garbage extracted for the grease which it may contain. The pressed and dried material has practically no value from its nitrogen or phosphorous content although the tankage is very heavy in soluble material.

These methods of calculation of formulæ are simply given as examples; as a matter of fact, probably not over 5 per cent of all the complete fertilizer manufactured contains "Filler" in the sense in which it is given above. When low-grade fertilizers are to be made, they are compounded from low-grade raw materials that will, without the use of fillers, or with only a very small amount, give the formula desired.

Peat Filler. Dried humus or peat is used as a filler on account of its absorbent properties. Its use was prohibited by some states as it was claimed that the nitrogen content included in the nitrogen of the fertilizer was unavailable. Within the last few years it has been determined by

experiment that while the nitrogen of peat may not show a high availability in the laboratory, actual growing experiments have demonstrated that peat is a very valuable fertilizer material and that the nitrogen becomes available in some manner in the soil. The South Carolina Experiment Station were the first to demonstrate this and as a result of their work and other work that has been done by investigators, the embargo has been lifted from peat and it is admitted into all states as a fertilizer with full credit for its nitrogen content.

CHAPTER XIX

ORGANIC CHEMICALS AND INTERMEDIATES

ALLEN ROGERS

Acetic Acid, CH_3COOH. Pure acetic acid is a colorless liquid, which, at 16° C., forms a solid known as *glacial acetic acid*. It is obtained from the dry distillation of wood. The distillate is treated with lime to produce calcium acetate, known commercially as *gray lime*. This gray lime, when heated with an acid, usually hydrochloric, gives acetic acid as a distillation product. Sugar is another source of acetic acid, the latter being formed when the sugar undergoes acid fermentation. On account of the enormous demand for acetic acid during the past few years, several plants have been built to manufacture acetic acid from vinegar and wine. The output of these plants now equals that obtained from dry distillation.

Acetic acid finds application in the printing and dyeing of wool and silk with acid and alizarine colors; in the scrouping of silk; in making fruit esters, in the manufacture of certain dyestuffs and coal tar products, and in the formation of acetates with the metals. The greatest demand, however, is in the manufacture of amyl acetate, a solvent for gun cotton; and for the non-inflammable cellulose acetate, used for moving picture films and as a coating for the wings of air planes.

Acetic Anhydride, $(CH_3CO)_2O$. This compound is obtained by the dehydration of acetic acid. It finds application in the preparation of alkyl acetates. It is manufactured by heating fused sodium acetate with acetyl chloride.

Acetanilide, $C_6H_5NHCH_3CO$. This compound is prepared by heating together a mixture of aniline and acetic acid for about 15 hours. It is a white crystalline compound slightly soluble in cold water, but very soluble in hot water. As it has the property of lowering the temperature of the animal body, it finds application in medicine as an antipyretic. Industrially it is used as a stabilizer of hydrogen peroxide, and as an intermediate for making certain dyestuffs.

Acetone, CH_3COCH_3. This compound is obtained to some extent from the dry distillation of wood, but commercially it is prepared by heating calcium acetate, *gray lime*, at a temperature of about 300° C. It is used as a solvent for the gums and fats, for *pyroxylene*, and in the extraction of tannin from gall nuts.

Acetylene, CH : CH. This compound is prepared by treating calcium carbide with water. It is a colorless gas used in illumination and exten-

sively in oxy-acetylene welding. It combines with copper, silver, and other metals, forming a class of very unstable compounds known as *acetylides.*

Acetyl Chloride, CH_3COCl. This compound is prepared by treating acetic acid with phosphorus trichloride. It is a colorless liquid, fuming in moist air, and is applied in organic synthesis, since it readily produces acetyl derivatives.

Alizarine, $C_6H_4(CO)_2C_6H_2(OH)_2$. This compound up to 1868 was obtained from madder, until Graebe and Lieberman made and brought forward their epoch-making discovery that it could be prepared synthetically from anthracene. It is chemically a dihydroxyanthraquinone. Since this discovery the synthetic compound has entirely replaced the natural product and has led to the discovery of many other alizarine dyestuffs. Its method of manufacture consists in heating together in an autoclave a mixture of sodium anthracene sulphonate and a solution of potassium chlorate. On cooling, the mass is extracted with boiling water, and the alizarine separated by adding hydrochloric acid. Alizarine comes on the market both in the crystal form and as a heavy paste.

Amyl Acetate, $CH_3COOC_5H_{11}$. This compound is prepared by treating amyl alcohol with fused sodium acetate in the presence of sulphuric acid. It is a liquid boiling at 148° C. and is used as a solvent for gun cotton in making the so-called *banana oil* or *bronzing liquid.* Until the pure food law went into effect it was also used in making artificial fruit essences.

Amyl Alcohol, $C_5H_{11}OH$. This alcohol is known in eight isomeric forms, but only a few have commercial application. They occur in the *fusel oil* obtained from the distillation of fermented grain.

Aniline, $C_6H_5NH_2$. This compound is prepared by reducing nitrobenzene with nascent hydrogen. It is a colorless liquid when freshly prepared, but turns dark on exposure to light, and boils at 183° C. It is used as a raw material in the manufacture of many dyestuffs, the so-called *aniline* colors. On a commercial scale the nascent hydrogen is obtained by heating the nitro product with iron filings to which a small quantity of hydrochloric acid has been added. At the end of the reaction the excess of acid is neutralized by adding milk of lime, and the resulting product steam distilled. The aniline, being heavier than water, settles to the bottom as a heavy, oily liquid.

Anthracene, $C_6H_4(CH)_2C_6H_4$. This compound occurs in coal tar from which it is obtained as colorless crystals by distillation. It is used in the manufacture of anthraquinone and alizarine.

Anthraquinone, $C_6H_4(CO)_2C_6H_4$. This product is manufactured from anthracene by heating it with a mixture of acetic acid and chromic acid. On throwing the mass into water, the anthraquinone separates as a brown powder which, after washing, may be purified by sublimation.

Benzaldehyde, C_6H_5CHO. This compound occurs in bitter almonds

in the form of a glyceride. It is a colorless liquid with a pleasant odor. Commercially it is prepared from benzyl chloride by heating it for some time with a solution of copper nitrate. The reaction product is extracted with ether and purified by means of sodium bisulphite and sulphuric acid, followed by steam distillation.

Benzene, C_6H_6. This compound occurs in coal tar, from which it is obtained, by distillation, as a colorless liquid having a boiling-point of 80.4° C. It is used to some extent as a solvent for gums and fats, but its principal application is as a raw material for the manufacture of benzene derivatives, used in medicine or for the manufacture of dyestuffs, phenol and explosives.

Benzidine, $NH_2C_6H_4—C_6H_4NH_2$. This compound is prepared by reducing para-dinitrodiphenyl with zinc dust in an alkaline solution. It is a colorless, crystalline body, employed extensively in making substantive dyestuffs. On a commercial scale, it is manufactured by heating, with reflux condenser attached, a mixture of caustic soda, ethyl alcohol, and nitrobenzene. The product of this reaction is then treated with zinc dust. When thrown into water, the excess of zinc dust and hydrazobenzene separate, which, on treatment with sulphuric acid and subsequently with caustic soda, yield pure benzidine.

Benzoic Acid, C_6H_5COOH. This compound occurs in gum benzoin from which it may be obtained by sublimation. It is prepared commercially from benzyl trichloride by heating with milk and lime. It is applied in medicine as a food preservative, in the form of the sodium salt in certain dyestuffs, and in seasoning tobacco.

Butyric Acid, C_3H_7COOH. When butter becomes rancid this acid is produced. It is also prepared commercially. It is a colorless liquid and is used to quite an extent in the form of its salts.

Chloroform, $CHCl_3$. This compound is obtained by treating alcohol or acetone with chloride of lime or by reducing carbon tetrachloride with hydrogen. It is also prepared electrolytically. It is a colorless liquid with a sweetish odor. It is used to some extent as a solvent, but mostly finds application as an *anæsthetic.*

Coumarine, $C_9H_6O_2$. This compound occurs in tonka bean and is also prepared synthetically. It is used in flavoring extracts and as tobacco flavor.

Dimethyl Aniline, $C_6H_5N(CH_3)_2$. A mixture of aniline, aniline hydrochloride, and methyl alcohol is heated in an autoclave for eight hours at 230°–240° C. The product is then made alkaline with caustic soda and steam distilled. It is used as an intermediate in the manufacture of certain dyestuffs.

Ether, $(C_2H_5)_2O$. This compound is prepared by treating alcohol with sulphuric acid in the proper proportion to form ethyl hydrogen sulphate. The latter is then heated in an iron still to a temperature of 140° C., and to it is added an equal quantity of alcohol, which combines with the ethyl hydrogen sulphate, producing ether and free sulphuric acid;

on addition of more alcohol, more ethyl hydrogen sulphate is formed and the cycle repeated. Ether is a colorless liquid, boiling at 34.9° C. Mixed with air and ignited, it combines with explosive effect. It is used as an anæsthetic, and also finds extensive industrial application in the manufacture of artificial silk, of collodion, and as a solvent for gums, fats, and waxes.

Formic Acid, HCOOH. This acid occurs in certain ants, bees, and in the hairs of the nettle. It is prepared commercially from sodium formate and sulphuric acid, the formate being produced by heating sodium hydroxide under pressure in the presence of carbon monoxide. Pure formic acid is a colorless liquid with a very pungent odor, and boils at 99° C. It is used in dyeing and as a deliming and plumping agent in the manufacture of leather.

Formaldehyde, HCHO. Formaldehyde is a colorless gas. Since it is very soluble in water it comes on the market as a 40 per cent solution under the name of *formalin.* It is obtained by passing the vapor of methyl alcohol over heated platinized asbestos. Besides being one of the best disinfecting agents known, having a high value as a germicide, it is also used as a fungicide on vegetable and plants. Combined with phenol and cresol, it forms important condensation products. The two principal ones on the market are *bakelite* and *condensite.* These appear not only in the form of varnishes, but, when run into molds and heated under pressure, they give substitutes for hard rubber, amber, and plaster, used for a variety of purposes from pipe stems and hair combs to electrical insulating boards. Another condensation product of this nature, known as *neradol,* finds application in the manufacture of leather.

Glycerine, $C_3H_5(OH)_3$. Glycerine results as a by-product in the manufacture of soap and candles. On account of the great demand for this material for munition purposes, many attempts have been made to produce it synthetically. Glycerine is a colorless, heavy liquid and is described at length in Chapter XXIX.

Hydroquinone, $C_6H_4(OH)_2$. P-dioxybenzene is a crystalline solid melting at 169° C. It is produced by reducing quinone with sulphuric acid. The hydroquinone is extracted from the aqueous solution by shaking with ether and the product purified by passing through animal charcoal and then recrystallizing. Hydroquinone is used as a "developer" in photography, and as an antifermentative and antipyretic agent in therapeutics.

Lactic Acid. This acid occurs in four isomeric forms. The ordinary acid, however, is found in sour milk and is manufactured on a commercial scale by treating glucose solution with the *lactic acid bacillus.* As the acid forms, it is neutralized with lime, and from the calcium lactate, the concentrated acid is obtained by treatment with sulphuric acid. Lactic acid is used to quite an extent in dyeing and in certain operations during the manufacture of leather.

Methyl Alcohol, CH_3OH. This compound, also known as *wood alcohol*, is obtained from the destructive distillation of wood. When pure it is a colorless liquid boiling at 66° C. It is used in the preparation of formaldehyde, as a solvent for gums in varnish making, in the manufacture of dyestuffs, for denaturing grain alcohol, and for many other purposes.

Naphthalene, $C_{10}H_8$. This compound occurs in coal tar, from which it is separated by sublimation as a white crystalline solid. It is used extensively in the preparation of dyestuffs, for the manufacture of phthalic anhydride, and as an antiseptic and moth preventative.

Naphthalene-β-Sulphonic Acid. Powdered naphthalene is added to warm concentrated sulphuric acid, and the mixture heated at 170° C. for about twelve hours. On cooling, the reaction product is poured into water, brought to a boil, and neutralized with milk and lime. The calcium sulphate separating is removed by filtration and the filtrate evaporated to a small volume. The calcium salt which crystallizes is separated, redissolved in water, and sufficient sodium carbonate introduced to convert all of the calcium to calcium carbonate. On again filtering and evaporating, the sodium salt of naphthalene-β-sulphonic acid crystallizes out. This product acts as an intermediate in the manufacture of β-naphthol.

Naphthol, $C_{10}H_7OH$. There are two naphthols, α and β, formed as white crystalline solids by heating their corresponding sulphonic acids with caustic soda. They are used very extensively in the manufacture of dyestuffs, and especially as developers for diazo colors. In making the β-naphthol, caustic soda is dissolved in water, then heated to about 280° C., and to it is added the sodium salt of naphthalene-β-sulphonic acid. Frothing of the mass indicates the completion of the reaction, and, in a molten state, it is poured on shallow pans. When cold, it is broken up and dissolved in boiling water. To the solution is added hydrochloric acid, which precipitates the β-naphthol. The crude product is filtered at the pump, dried, and distilled in vacuum.

Nitraniline, $C_6H_4NH_2NO_2$. By introducing the nitro group into aniline three substitution products are obtained. *Para-nitraniline* is the most important and finds extensive application as a raw material for producing *para-red*. This compound is formed by first diazotizing the para-nitraniline and then developing with beta-naphthol.

Nitrobenzene, $C_6H_5NO_2$. When benzene is treated with fuming nitric acid, a heavy, yellow, oily substance results. This substance, known commercially as *oil of mirbane*, has an odor resembling bitter almonds. It is used as a soap perfume, for hiding odors, and in the manufacture of aniline.

Oleic Acid, $C_{17}H_{33}COOH$. This acid in the form of glyceride occurs abundantly in fats and oils, from which it may be separated by saponification and subsequent treatment with sulphuric acid. It is used in the

manufacture of oil soluble colors and of soft soaps. By treating with hydrogen in the presence of nickel it is readily transformed into stearic acid.

Oxalic Acid, $(COOH)_2$. The old way of making this compound was to beat a mixture of sawdust and caustic soda together at a temperature of about 240° C. The mass thus formed was extracted with water, evaporated, and treated with milk of lime. The calcium oxalate, on being treated with sulphuric acid and again evaporated, gave the oxalic acid. At present it is made by the Goldschmidt process, which consists in heating a mixture of potassium formate or carbonate with a little potassium oxalate and a slight excess of caustic alkali. It has recently been discovered that sodium can be used in place of potassium. The oxalic acid is then freed from this mass by means of sulphuric acid. It forms transparent crystals having two molecules of water. It is used in dyeing and printing, as a bleach for straw and leather, and for purifying glycerine.

Phenol, C_6H_5OH. This compound occurs in coal tar, from which it is separated by distillation as a colorless crystalline mass that melts at 42.5° C. Inasmuch as the supply of phenol from this source is limited, it has become necessary to produce it synthetically by fusing sodium benzene sulphonate with caustic soda and then neutralizing with hydrochloric acid. Phenol is used as an antiseptic, for making picric acid, for the manufacture of certain dyestuffs and pharmaceutical products and with formaldehyde in many condensation products.

Picric Acid, $C_6H_2OH(NO_2)_3$. This compound is prepared by treating phenyl sulphonic acid with nitric acid. It forms yellow crystals, used to some extent in dyeing. Some of its salts find application in the manufacture of explosives.

Pyridine, C_5H_5N. This compound is obtained from the dry-distillation of bones as a yellow oil with a very disagreeable odor. It is used in the denaturing of alcohol.

Pyrogallol, $C_6H_3(OH)_3$. By heating gallic acid with water under pressure this compound results. It is a white crystalline powder used in photography as a developing agent, and for absorbing oxygen in gas analysis.

R Salt (**β-Naphthol 3 : 6 Disulphonic Acid**). A mixture of β-naphthol and sulphuric acid is heated to 125° C. and the reaction product dissolved in water. The excess of acid is neutralized with lime and the calcium salt decomposed with sodium carbonate. The R Salt is separated from the filtrate by crystallization.

Resorcinol, $C_6H_4(OH)_2$. This is prepared from meta-benzene disulphonic acid by heating with caustic potash. It is a white crystalline compound and is used in the manufacture of dyestuffs.

Saccharine, $C_6H_4\begin{<}{CO}{SO_2}\end{>}NH$. This compound is the imido derivative of ortho-sulphobenzoic acid. It is a white crystalline powder said to

be 500 times sweeter than sugar. It has no food value, but is used on account of its great sweetening power.

Salicylic Acid, $C_6H_4OHCOOH$. This compound is prepared by heating sodium phenoxide in the presence of carbon dioxide to a temperature of 140° C. From the sodium salicylate thus formed the acid is obtained by treatment with sulphuric acid. It forms white crystals, used as an antiseptic, for food preservation, in the manufacture of dyestuffs, for perfumery, and in medicine.

Schaeffer's Salt (β-Naphthol-6-Sulphonic Acid). This important intermediate is prepared by heating β-naphthol with sulphuric acid. The product of the reaction is salted out and filtered at the pump.

Stearic Acid, $C_{17}H_{35}COOH$. This compound occurs as a glyceride, mixed with other fatty acids, in many fats and oils. It is usually prepared from beef tallow by saponification and subsequent treatment with sulphuric acid. The stearic acid, having a high melting-point, readily separates from the softer fatty acids present. It is used in candle making, for soap manufacture, and for other purposes.

p-Sulphanilic Acid, $C_6H_4NH_2HSO_3$. This compound is prepared by heating aniline with sulphuric acid to a temperature of 200° C. It forms a white crystalline powder much used in the preparation of dyestuffs and diazo colors.

Tannin, $C_{14}H_{10}O_9$. Tannin occurs very widely in nature as a constituent of many barks, leaves, and woods. Its water extract is employed in the manufacture of leather and as a mordant in dyeing cotton with basic colors. In a pure condition it may be obtained from nut-galls by extracting with acetone-alcohol mixture and comes on the market as a light yellow powder. When brought in contact with iron a black precipitate is formed which finds application in the manufacture of writing inks. It also combines with other metals forming different colored *lakes*.

Tartaric Acid, $C_4H_6O_6$. The ordinary tartaric acid occurs as crude tartar, a by-product from the manufacture of wine. There are four isomeric forms of this acid, but the one known as dextro-tartaric acid is that most commonly used. It forms many salts which have a wide application, the most common being potassium hydrogen tartrate or *cream of tartar*, $KHC_4H_6O_6$.

Thymol, $(CH_3)_2CHC_6H_2(CH_3)_2OH$. This compound occurs in oil of thyme and is used as an antiseptic and as treatment for the hookworm disease.

Toluene, $C_6H_5CH_3$. This compound occurs in coal tar, from which it is recovered by distillation as a colorless liquid, boiling at 111° C. It finds application as a solvent, but its principal use is as a raw material for the manufacture of dyestuffs, and the explosive, trinitrotoluene, T.N.T.

Xylene, $C_6H_4(CH_3)_2$. This compound occurs in coal tar, from which it is separated by distillation as a colorless liquid. It has three isomeric forms and is used in the manufacture of dyestuffs.

CHAPTER XX

ILLUMINATING GAS

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Classification. The industrial gases in use at the present time may be divided, roughly, into three general classes—coal and carburetted water gas and their various mixtures; the different classes of oil gas, acetylene, gasoline gas; and producer gas. The first class is by far the most important from an illuminating standpoint, while producer gas is, of course, of the greatest importance for fuel and power use. The other gases are generally employed in special cases where the use of the first class is impossible or inconvenient.

Development. In the earlier days of the industry, gas was employed primarily as an illuminant, and at the present time the illuminating value is still the standard prescribed in many of our larger cities, yet within the last decade the regulations of the Public Service Commissions have almost entirely eliminated the test for illuminating value and substituted the heating value as the statutary standard. To date (May, 1917) seventeen States have adopted the heating value standard, the average requirement being 575 B.T.U. Total heating value per cubic foot for a monthly average.

This change, which started in England and Germany, has been due to several causes, among which may be mentioned the great increase in the use of mantle burners and the increasing use of gas for fuel purposes.

The report of the Geological Survey for 1915 indicates that about 30 per cent of the gas consumed is used for illumination, 48 per cent for domestic fuel and 22 per cent for industrial fuel.

The enormous expansion in certain industrial work as a result of the demand for munitions and other supplies has resulted in a very great expansion in the use of gas furnaces for the manifold processes where very accurate temperature regulation was absolutely essential. This has brought out most forcibly the many advantages of gas as an industrial fuel and will undoubtedly result in increasing its future use by bringing it to the attention of many trades that had heretofore been too conservative to adopt it.

Since the figures of the last census are now so hopelessly cut of date, the following figures taken from Mineral Resources will give some idea of the present status of the industry.

STATISTICS OF THE GAS INDUSTRY, 1915

Coal gas	43,747,432,000 cu.ft.
Coke oven gas	84,355,914,000
Water gas	124,129,569,000
Oil gas	13,971,333,000
Total	266,204,248,000 cu.ft.

RELATIVE USE

	For Illumination.	For Fuel.
1905	74%	26%
1915	30	70

RAW MATERIALS EXCLUDING COKE OVENS

Gas coal	4,645,000 tons
Anthracite coal	830,519 tons
Coke	1,318,226 tons
Gas oil	690,955,000 gallons

BY-PRODUCTS EXCLUDING COKE OVENS

Coke	2,941,000 tons
Coal tar	51,845,400 gallons
Water-gas tar	50,747,300 gallons
Light oils and condensate	1,316,527 gallons
Ammonia as ammonium sulphate	52,311 tons

PROCESSES EMPLOYED

Coal gas	396 plants
Water gas	553 plants
Oil gas	93 plants

Total number of plants is 917; there are a number of plants employing two processes.

Constituents of Illuminating Gas. Commercial gases consist of mixtures, in varying proportions, of the gases or vapors whose characteristics are shown in the table on the following page.

In addition to the constituents shown in this table, there always exists in the crude gases, before purification, traces of ammonia and other organic compounds, but the above mentioned constituents may be considered as those important to the industrial chemist.

The relative occurrence of the commoner constituents in some of the many varieties of commercial gases is given in the table below. These typical analyses must not be considered as standards, but as rather expressing the average composition of commercial samples obtained under certain conditions with the process mentioned.

PROPERTIES OF THE IMPORTANT CONSTITUENTS OF COMMERCIAL GASES [1]

Name.	Specific Gravity.	Weight per Cu.ft. Lbs.	Specific Heat.	Heating Value B.T.U. per Cu.ft.	Heat of Formation B.T.U. per Lb.	Air Required for Combustion.		Flat Flame Candle Power Burned at 5 Cu.ft. per Hour.
						Cu.ft., per Cu.ft.	Lbs. per Lb.	
Benzol	2.6953	.20640	.3754	3700.3	− 229.3	35.888	13.313	350–420
Toluene	3.1792	.24345	....	4448.7	− 68.8	43.065	13.547	
Xylene	3.6630	.28050	....	5165.1	+ 257.4	53.240	13.720	
Ethylene	.9676	.07410	.4040	1588.0	− 174.2	14.355	14.836	68.5
Propylene	1.4514	.11115	....	2347.2	+ 138.0	21.533	14.836	
Butylene	1.9353	.14820	....	3099.2	+ 342.6	28.710	14.836	
Hydrogen	.0692	.00530	3.4090	326.2	.....	2.393	34.624	
Carbon monoxide	.9671	.07407	.2450	323.5	+1869.2	2.693	32.471	
Methane	.5529	.04234	.5929	1009.0	+2435.6	9.570	17.312	5.2
Ethane	1.0368	.07940	.7070	1764.4	+1713.6	16.748	16.156	35.7
Carbon dioxide	1.5195	.11637	.2163	.....	+3979.1			
Oxygen	1.0152	.08463	.2174					
Nitrogen	.9701	.07429	.2438					
Air	1.0000	.07658	.2374					
Steam	.6217	.04761	.4805	.....	+6870.4			
Hydrogen sulphide	1.1769	.09012	.2423	672.2	+ 250.9	7.178	6.111	
Ammonia	.5888	.04509	.5083	432.8	+1259.0	3.589	6.111	
Cyanogen	1.8000	.13779	.2615	1238.2	−2273.9	9.570	5.323	
Carbon disulphide	2.6298	.20139	.1590	1264.6	−6160.0	14.355	5.466	

[1] The data given are calculated to 60° F. and 30.0″ Barometer.

The English units, i.e., pounds, Fahrenheit degrees, and feet, since they are customary in the gas industry, are used in this chapter.

AVERAGE COMPOSITION OF COMMERCIAL GASES

	Ill,s %	CO %	H_2 %	CH_4 %	C_2H_6 %	CO_2 %	O_2 %	N_2 %	Candle Power.	B.T.U.
Coal gas	4.0	8.5	49.8	29.5	3.2	1.6	.4	3.2	16.1	622
Carburetted water gas	13.3	30.4	37.7	10.0	3.2	3.0	.4	2.1	22.1	643
Pintsch gas	30.0	.1	13.2	45.0	9.0	.2	.0	1.6	43.0	1276
Blau gas	51.9	.1	2.7	44.1	.0	.0	.0	1.2	48.2	1704
All oil water gas	7.0	9.2	39.8	34.6	.....	2.6	.2	6.6	19.7	680
Acetylene gas	96.0	....	....	.....	.....	....	.8	3.2	225.0	1350
Gasoline gas	1.5	....	....	C_6H_{14} = 10.3			18.5	69.7	16.0	514
Oil gas	31.3	2.4	13.5	46.5	3.9	.3	.0	1.1	38.0	1320
Blue water gas	.0	40.9	50.8	.2	.0	3.4	.9	3.5	.....	299
Balloon gas	.4	5.2	75.4	10.4	.0	1.0	.6	.7	.....	375
Methane-hydrogen gas	3.0	15.0	64.2	12.0	.0	2.3	.2	3.0	11.0	400
Producer gas (coal)	.2	17.6	10.4	6.3	.0	7.3	.7	58.1	.....	161
Producer gas (coke)	.0	25.3	13.2	.4	.0	5.4	.6	55.2	.....	137
Blast furnace gas	.0	26.5	3.5	.2	.0	12.8	.1	56.9	.....	100
Wood gas (pine)	10.6	27.1	32.7	21.5	.....	4.9	.4	2.6		607

In general, then, we may say that the commercial gases are mixtures of gases, hydrocarbons and vapors, together with certain permanent gases produced by the pyrodecomposition and polymerization of complex hydrocarbon mixtures or compounds either alone or in the presence of air and steam.

Manufacture of Coal Gas. Coal gas is the result of the destructive distillation of bituminous coal in highly heated fireclay or silica retorts. The retorts vary considerably in cross-section, length and method of heating. They are usually set in groups of from six to nine retorts in what is known as a "bench," and the group of "benches" varying with the capacity of the plant is known as the "stack." In a few of the older and smaller plants the retorts are heated by a direct fire of coke or coal, but in the more modern and larger plants they are heated with producer gas. These retorts may be set either in a horizontal or inclined position. The object, however, in any case is to drive off the volatile matter which consists principally of gas. Other products are also eliminated, and will be considered in due course of time.

The manufacture of coal gas thus consists in the transformation of the potential energy of a set of solid hydrocarbons into the more convenient gaseous form by means of dry distillation. Murdock, who is probably the inventer of coal gas, distilled the coal in a simple iron pot over a fire, and to a certain extent this is still the basic principle of our present day practice.

Many other methods of carbonizing have been proposed and tried. These may be classed under three heads, viz.: (*a*) the use of internally heated vessels; (*b*) the use of a body of ignited coke; and (*c*) the use of hot gas as a heat carrier.

Many patents have been taken out and a great deal of experimental work has been done in endeavoring to perfect processes that would utilize these principles, but in general they have failed to produce a gas that could commercially compete with that produced in the usual system of carbonizing the coal in an externally heated retort. The principal causes of their failure have been the time required for the complete distillation of the coal and the poor quality of gas produced, due, generally, to its decomposition in the presence of the high temperatures that were necessarily employed.

There are three general methods by which the distillation of coal in externally heated closed retorts is carried on:

First, the use of relatively small charges of coal which do not completely fill the enclosing retort, leaving a variable free space at the top. This would represent the usual horizontal or inclined retorts.

Second, the use of relatively large thick charges of coal which do not completely fill the retort and leave a free space at the top, such as a chamber or coke oven.

Third, the use of vertical retorts where the whole periphery is heated

and filled with the charge, but there may or may not be a free space above the charge at the top of the retort. This type includes the various continuous or intermittently charged vertical retorts and some of the modifications of the vertical coke oven.

Fig. 198 is a sectional elevation of a bench of through "mines."

The retorts in the stop end bench are of fireclay 9 feet long of D section 16 by 26 inches and are 3 inches thick, in the through bench the retorts are 20 feet long.

The retorts are provided with an iron mouthpiece with a self-sealing door operated by a system of eccentric cams and levers.

It will be noted that the stop end retorts have only one mouthpiece while the "throughs" have two, one at each end.

From the mouthpiece the gas passes up through what is known as an ascension pipe to the bridge pipe and thence down through the dip pipe into the hydraulic main.

When the benches are operated at very high temperatures to secure the maximum yield of gas, and especially with certain coals, the ascension bridge and dip pipes became choked with a hard carbonaceous deposit that is sometimes very difficult to remove. Removable covers are provided to so arrange that cleaning tools may be used to remove these deposits. Many schemes have been devised to remedy this difficulty. One consists in arranging three retorts in a vertical plane and using a single straight ascension, or as it is frequently called, stand pipe; this is then cleaned with a mechanically driven auger. Another device connects the retorts by a side connection with a large rectangular stand pipe provided with internal slide valves for each retort and down which a stream of water or weak ammoniacal liquor is constantly circulated being removed by a sealed overflow tank at the bottom. This latter device appears to entirely eliminate all difficulty from stoppage.

The hydraulic main is now usually made of steel plate, is either round or "*D*" shaped and is filled to a fixed level with ammoniacal liquor so that the end of the dip pipes are sealed by the liquor, thus preventing the escape of the gas while the retort is being charged, and at the same time allowing the gas to freely enter the hydraulic main.

In the older installations the hydraulic main was usually continuous, running the entire length of the stack. This arrangement frequently gave trouble, due to uneven settling of the bench construction throwing it out of level. In the later construction each bench has an individual small main.

In many later plants an automatic device is used whereby the level of the liquor in the hydraulic main may be raised, thus sealing the dip pipes when the retorts are to be charged, or put out of service for any reason. Then by pulling a lever the level is dropped below the dip pipes, thus putting the retorts in direct connection with the discharge pipes and eliminating the vibration set up by the passage of the gas through the water seal.

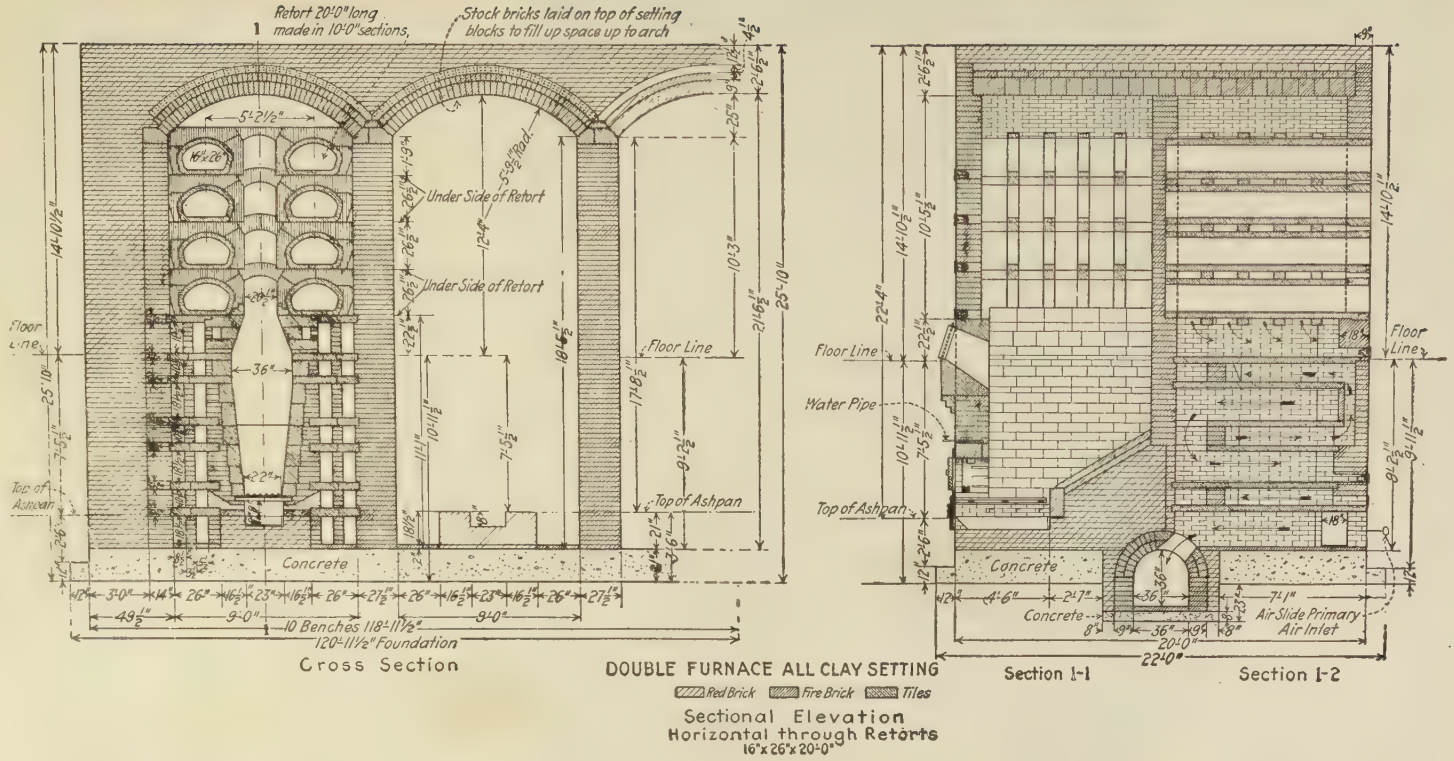

Retort 20'0" long made in 10'0" sections.
Stock bricks laid on top of setting blocks to fill up space up to arch
Under Side of Retort
Under Side of Retort
Floor Line
Top of Ashpan
Floor Line
Top of Ashpan
Concrete
10 Benches 118'-11½" 9'-0"
120'-11½" Foundation
Cross Section
Floor Line
Water Pipe
Top of Ashpan
Concrete
Concrete
Air Slide Primary Air Inlet
Section 1-1
Section 1-2
DOUBLE FURNACE ALL CLAY SETTING
Red Brick
Fire Brick
Tiles
Sectional Elevation
Horizontal through Retorts
16"x 26"x 20'-0"

FIG. 198.

From the hydraulic main the gas passes by means of a large pipe called the "foul main" to the condensing and purifying apparatus, which will be taken up later.

The producer is provided with grate bars and cleaning doors and is charged with hot coke as it is drawn from the retorts through the charging door on the upper floor level. The primary air enters through regulating shutters at the front of the bench, passes around the lower waste gas flues and hence beneath the grate. Rising through the fuel it combines

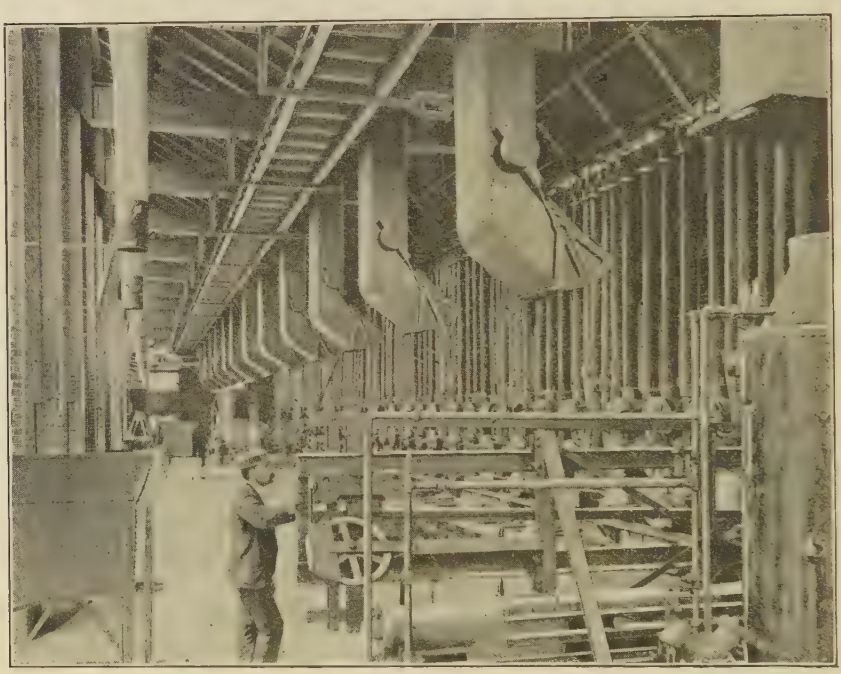


FIG. 199.—This illustration shows the conveyor as it passes over the retorts. The machine below is the Bronder Discharging Machine. This discharges three retorts simultaneously with "T" headed rakes, operated with a steam cylinder. Used for stop-end retorts.

with the carbon, forming producer gas. Steam is admitted beneath the grate to soften the clinkers and control their formation by lowering the temperature of the fuel bed. This is due to the endothermic nature of the reaction with the carbon of the fuel. Lately a process has been introduced in which a portion of the waste gases are returned beneath the grate with the primary air. The endothermic reduction of the carbon dioxide and the diluting action of the nitrogen thus serve to control the fuel bed temperature. With certain coals this has not been successful.

As the producer gas rises through the *nostrils* into the *combustion chamber* it meets the secondary air which is admitted through regulating shutters below and at the front of the bench. The air travels through

firebrick ducts in what is known as the *recuperator*, where it passes horizontally to the right and left and upward and is heated by the waste gases to a temperature of from 1600° F. to 1800° F., practically attaining the temperature of the waste gases.

As the combustion takes place the hot products of combustion rise around the retorts to the top of the combustion chamber and are then drawn down and toward the front of the bench where they enter the waste gas flues in the recuperator passing horizontally front and back and downwards giving up their heat to the incoming secondary and primary air. The waste gases finally pass to the back of the bench and hence to the stack, the draft of which is controlled with a damper set at a convenient point in the recuperator.

The temperature in the bench is regulated by a proper admission of primary air to the recuperator and adjusting the secondary air supply so that a slight excess of oxygen is present in the waste gases (about 1.0 per cent). The distribution of the heat is controlled by the stack draft which is usually so regulated that the pressure in the furnace is just at a balance. In the combustion chamber the temperatures will vary from 2800° F. to 3200° F., just above the nostrils to from 1900° F. to 2200° F. at the entrance to the recuperators. Where the products of combustion are used under the grate instead of steam these temperatures will be several hundred degrees lower. In the retorts the temperature will vary from 1600° F. to 1800° F.

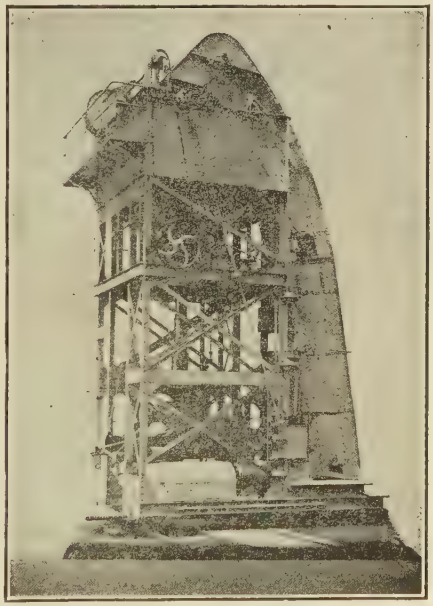


Fig. 200. — De Brower-Jenkins Centrifugal Charging Machine. Electrically operated. Has elevating conveyor to pick up coal from the charging floor level, which does away with elevated bins.

In the older plants the coal was charged into the retorts with shovels by hand and the coke withdrawn with iron rakes, but in the larger plants mechanical charging and discharging machines are used. Fig. 199 illustrates the Bronder type of discharging rake.

Fig. 200 is the De Brower type of centrifugal charging machine and Fig. 201 the discharging ram. Fig. 202 is the Fiddes-Aldridge type in which the coke is pushed out of the retort by the sectional scoop that introduces the fresh charge of coke. The West is another machine of this type.

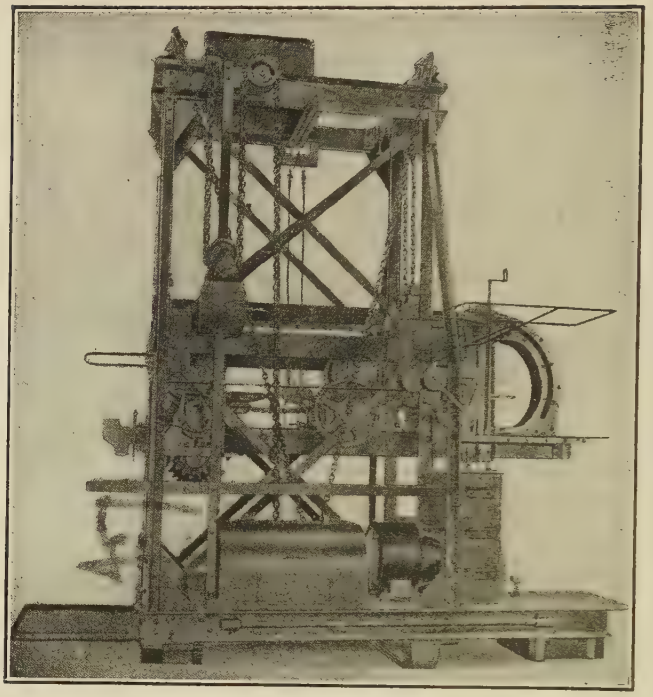


FIG. 201.—De Brower-Jenkins Discharging Ram. Electrically operated. Is raised and lowered to take retorts at different levels.

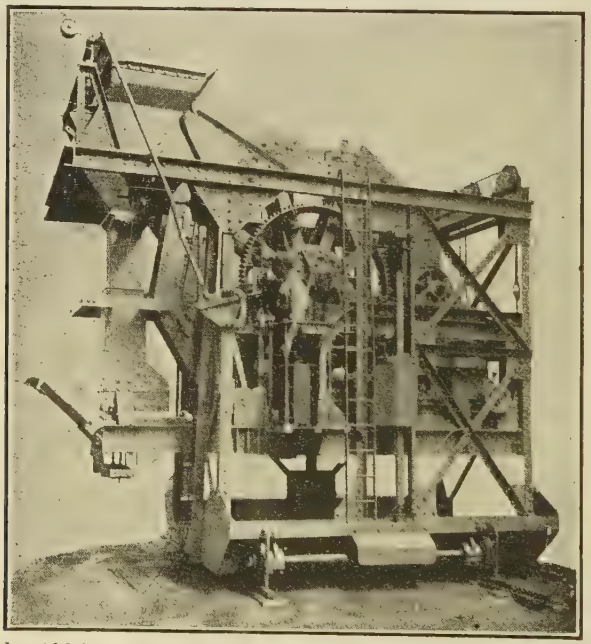


FIG. 202.—Fiddes-Aldridge One-stroke Machine. The charging scoop is sectional and pushes the coke out of one end of the retort as it enters with the fresh charge at the other end.

In endeavoring to reduce the labor and expense of charging the coal and removing the coke the inclined type of bench was introduced. In this type the retorts were set at about 32° to the horizontal. The coal

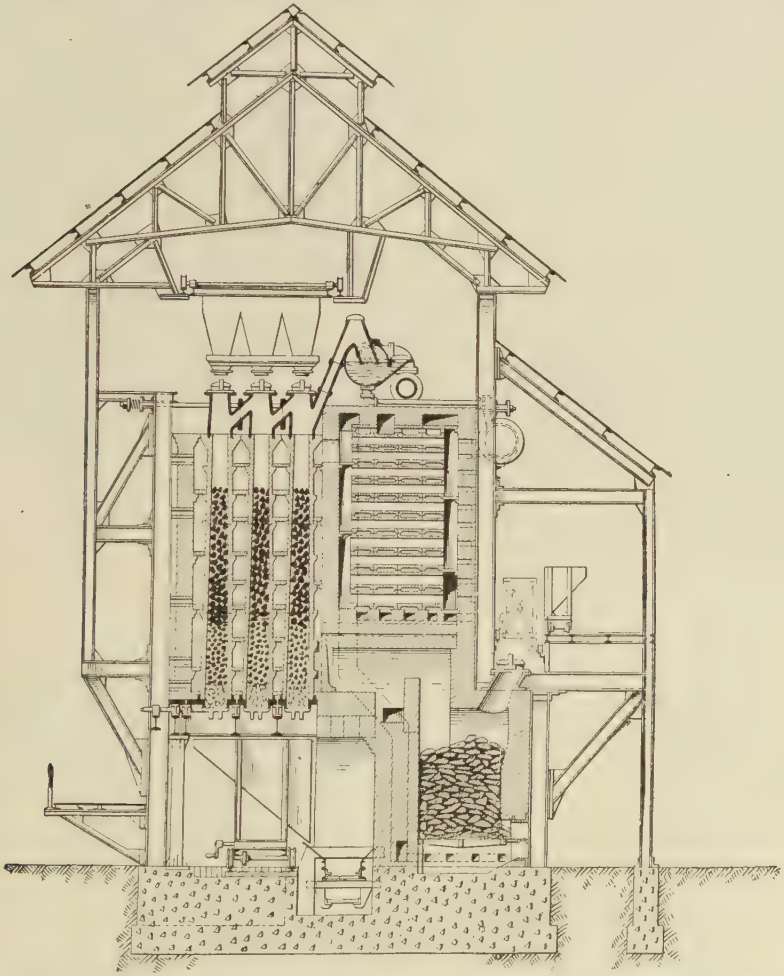


FIG. 203.—American Type of Vertical Retort. Nine retorts in bench. Retorts oval, 10″×14″ at top, 16″×22″ at bottom, 18′ 6″ long. One producer of large grate area. Primary and secondary air controlled with Venturi meters. Three retorts on one standpipe, which are charged and discharged at one time. Length of charge 9 hours, coal and coke handled by conveyors. Electrical operation.

is fed in at the top by gravity and since this is beyond the angle of repose for coke it will slide out of the retort at the bottom when set in motion after opening the lower lids. This type has not been used very extensively in the United States, as the vertical type is meeting with more favor.

Fig. 203 is an example of an American vertical retort bench. Here the coal drops into the retort from overhead bins and the coke drops out at the bottom, entirely eliminating manual handling. From the shape and position of the charge it produces a better quality of gas and coke, the gas rising through the center of the charge thus being protected to some extent from contact with the hot sides of the retort.

The simplicity of operation has led to the introduction of continuous systems of carbonization in which the coal is fed in at the top and the coke withdrawn continuously at the bottom of the retort by appropriate mechanical devices. Such a system is illustrated in Fig. 204, which is a cross-section of the Glover-West type. Another system is the Woodall-Duckham which differs somewhat in details.

In an endeavor to still further reduce operating costs the carbonization in large units has received considerable attention. Here the carbonizing chamber is enlarged to hold from three to eight tons of coal and is arranged horizontally, on an incline, or vertically. Fig. 205 is an exterior view of a Koppers Oven. Where illuminating gas is required appropriate arrangements are made in the heating flues to prevent overheating the gas as it leaves the top of the oven. The Munich Chamber Ovens may also be mentioned as an example of large scale carbonizing apparatus.

The general tendency in the later installations has been in the direction of carbonization in larger units. In the horizontal settings it has resulted in the more general use of "through" retorts. The vertical retort setting with its larger charge, lower and easier labor of operation, and greatly improved yield of gas and residuals, and especially the quality of coke produced, has increased rapidly. Some experimental installations of large inclined chambers have been made and several coke ovens (modified to avoid overheating the gas) have been put into operation.

It will be noted that all of these forms are heated by producer gas, generated either in producers built as an integral part of the bench or in separate plants. The proper and efficient operation of a producer, and the maintaining of a uniform and effective temperature in the carbonizing chambers, are the important factors in successful bench operation.

The advances that have been made in recent years in the efficiency of many of our manufacturing processes are based on the great advance in our knowledge of the mechanism of combustion, and in the refinements and methods for its accurate control.

The important factors in the operation of the producer are proper regulation of the drafts and the admission at a uniform rate of the requisite quantities of primary and secondary air required in order that a suitable temperature may be maintained, and to insure the efficiency of this combustion the flue gases must contain a high percentage of carbon dioxide. Accurate commercial instruments are now available for the determination and the control of all of these factors.

The introduction of external producer plants, where the gas is gen-

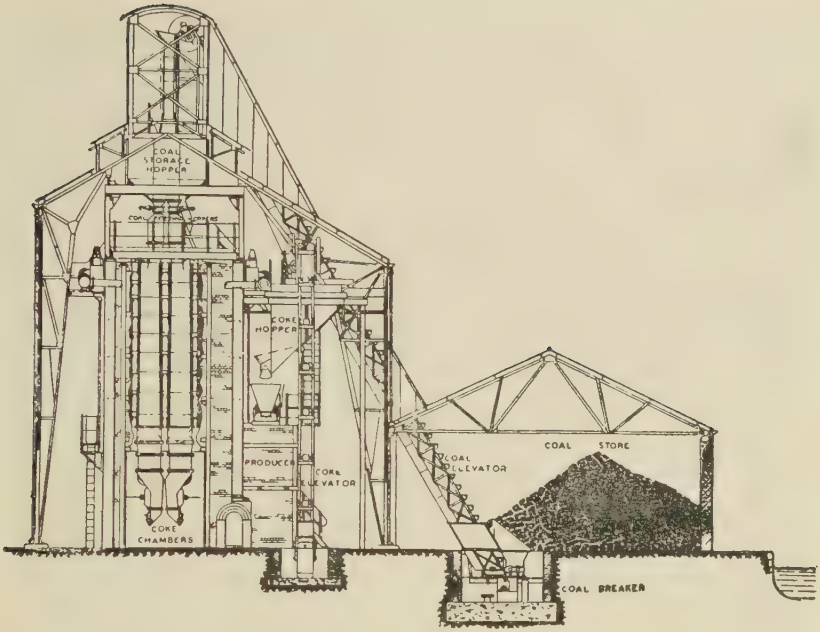


FIG. 204.—Glover-West Continuous Verticals. Sectional elevation of vertical retort house and coal stores. Eight retorts in a bench. Single producer. Retorts are heated by sections. Coal falls into retort by gravity as coke is removed from the bottom.

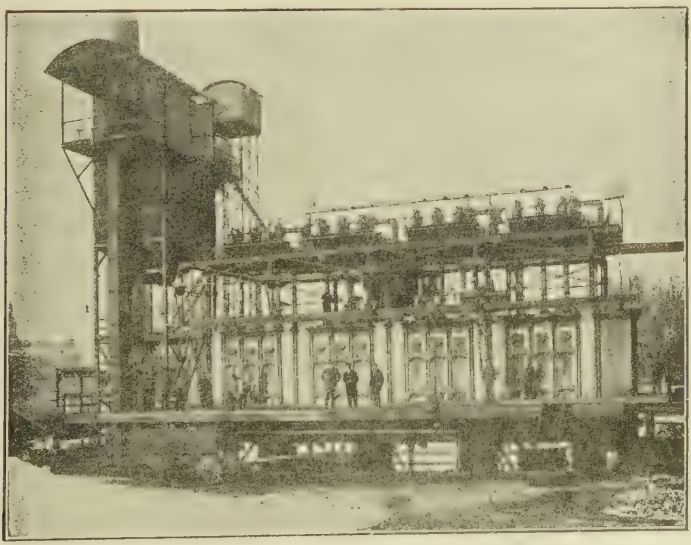


FIG. 205.—Kopper Coke Ovens. Three chambers heated by one generator. Chambers 14′ long, 8′ high, 17″×18½″ in width. Heating is by vertical flues. Each set of chambers has a separate hydraulic main. Chambers are charged from top of larry and the coke is pushed out with a ram. Charge is about four tons of coal

FIG. 206.—Unloading Coal at Dock and Dumping into Trucks.

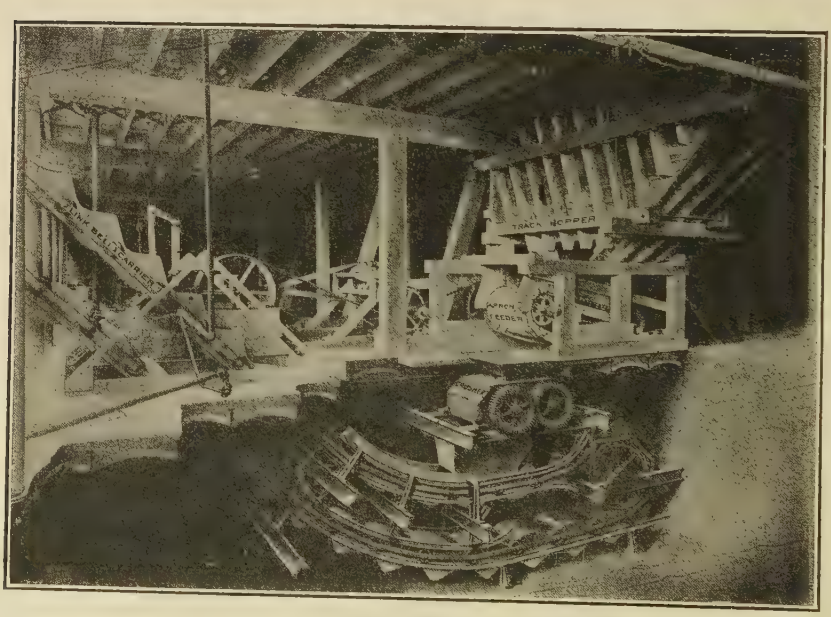


FIG. 207.—The coal having been dumped into hopper from trucks is crushed and transferred to bucket conveyors.

erated and partially purified before being admitted to the benches, seems to promise further economies in the fuel necessary to carry out the process of carbonization. Other mechanical devices have been introduced, such as rocking grates, which are designed to continuously remove the ash and thus result in more uniform fire conditions, and mechanical devices whereby the admission of the primary and secondary air may be controlled to correspond to the varying conditions of the fuel bed. The saving in fuel that has been effected by the use of more accurate control over the combustion is shown by the following table, where the fuel used in the producer, when calculated to pounds of coke per thousand feet of gas made, is compared:

Type of Bench.	Fuel in Lbs. per M feet Gas Made
Old type of direct fired	70 to 75 lbs.
Full depth recuperative bench without mechanical control	30 to 35 lbs.
Mechanically controlled benches	18 to 22 lbs.

Mechanical Coal and Coke Handling Devices. In the smaller plants the coal and coke is usually handled by hand in iron wagons known as "buggies," but with the increase in the size of the more modern plants

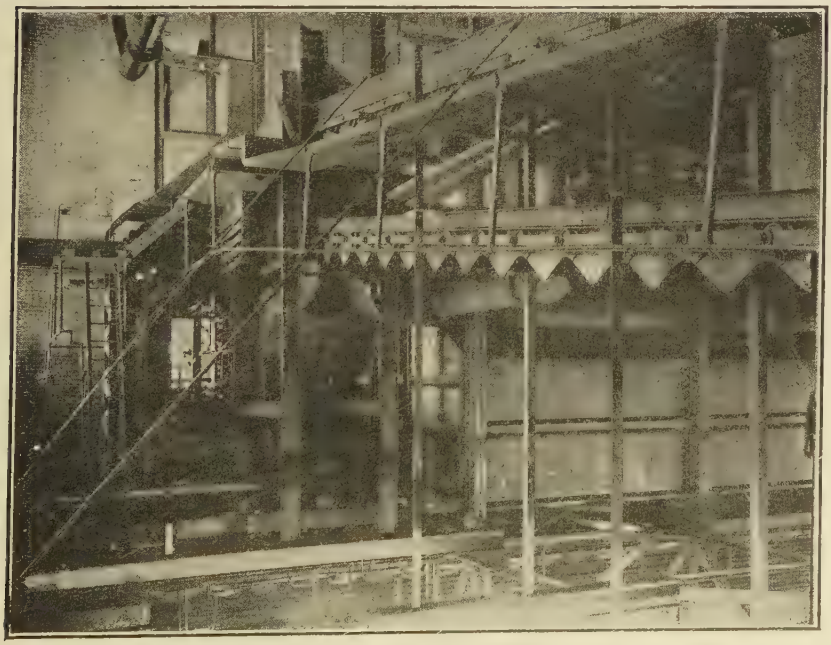


FIG. 208.—This illustration shows the buckets loaded and on their way to the storage bins.

mechanical methods soon became imperative not only on account of the difficulty and increased cost of obtaining the necessary labor but also on account of the enormous quantities of material to be handled, so that at present in the modern plants the coal and coke are handled entirely by machinery, and almost automatically.

Fig. 206 is an unloading installation that will put the coal in storage piles or in trucks. Telfer systems have been considerably used where the coal must be transported a considerable distance and the belt or bucket type of conveyor where the distance is short. Figs. 207 and 208 illustrate an installation of the bucket type. For coke the push-plate type of conveyor running in a trough seems to be most generally used. Where the coke is hot the trough is partially filled with water.

The use of mechanical devices in charging the coal into the retorts and removing the coke has already been mentioned.

Theory of Coal Carbonization. From the high temperatures and considerable amount of fuel that are employed in the distillation of coal we would expect to find an endothermic reaction, and it is still so considered by some. The work of Mahler, Euchane and others has shown that it is probably slightly exothermic. The heat given off by the distillation varies somewhat with the volatile content of the coal and other conditions, but averages about 350 B.T.U. per pound of coal.

The fuel used in carrying out the process serves to start the distillation and supply the sensible heat that is carried off by the evolved products.

From the heat balance that is given in the table it will be noted that the heat given off by the reaction is but a small fraction of the total heat involved and may be neglected.

HEAT BALANCE WITH A REGENERATIVE BENCH.

Per 100 lbs. of Coal Carbonized

Heat Produced		
By combustion of coke	180553	B.T.U.
By formation of volatile compounds	52637	"
Total heat evolved	233190	"
Heat Absorbed.		
As sensible and latent heat of flue gases	58734	B.T.U.
As sensible heat of gaseous vapors	32166	"
As sensible heat of coke	43148	"
As sensible heat of clinker	1863	"
By radiation	48276	"
By formation of volatile compounds	3517	"
By decomposition of coal	45486	"
Total heat absorbed	233190	"

PERCENTAGE DISTRIBUTION OF HEAT LOSSES

By flue gases	25.20%	
By volatile compounds	13.80	
By coke	18.50	
		57.50%
By radiation	20.70	
By formation of volatile compounds	1.50	
By decomposition of coal	19.50	
By clinker	.80	
		42.50%

It is interesting to note in this connection that in the example quoted the fuel used was at the rate of 30.2 lbs. per thousand cubic feet of gas made, almost exactly what we would expect in the manufacture of carburetted water gas where not only all the heat necessary for the reaction, but also about one-third of the total heat in the gas comes from the fuel.

The general course of the distillation of coal is influenced by a number of factors and these may be summarized into the general statement that under any given condition of temperature and pressure it is the rate at which the heat penetrates the coal particles and the time that the gaseous vapors are exposed to its influence that determines the course and results of the distillation.

The coal particles acquire the temperature of the retort by conduction, radiation, and from the passage of the heated vapors through the charge. The rate of carbonization toward the center of a charge has been estimated at from 1.0–1.5 inches per hour in horizontal retorts, 0.5–0.6 inch in vertical retorts, and from 0.3–0.5 inch in coke ovens. The factors that influence the rapidity of heating are the available heat, head, the size of the coal particles and the moisture content. In general, in order to secure the maximum increase in temperature the coal particles should be brought into intimate contact with the walls of the retort, and must provide a certain percentage of voids for the circulation of the heated gases, while an increase in the size of the coal particles up to a certain point generally yields improved results.

Gas Coal. In the manufacture of coal gas, coal with a high volatile content is generally preferred; that is, a coal belonging to the bituminous series according to the usual method of coal classification.

COAL CLASSIFICATION—GRUNER

	Carbon.	Hydrogen.	Oxygen.
Dry coal; long flaming, non-coking	75–80	4.5–5.5	15.0–18.5
Fat gas coal; porous, brittle coke	80–85	5.0–5.8	10.0–13.2
Semi-fat furnace coal; good coke but porous	84–89	5.0–5.5	5.5–10.0
Coking coal; best grade of coke	89–91	4.5–5.5	4.5–5.5
Lean and anthracite coals; non-coking	90–93	3.0–4.5	3.0–4.5

These methods of classification vary somewhat, but usually depend either on the ratio of volatile combustible to fixed carbon, or upon the ratio of hydrogen to carbon, as determined by ultimate analysis. Such a classification is given in the table on the preceding page.

The gas coals in general use have a volatile content running from 32 to 40 per cent or a carbon: hydrogen ratio of from $13\frac{1}{2}$ to 17. The analyses of a number of American coals are shown in the table:

PROXIMATE AND ULTIMATE ANALYSES OF GAS COALS

State. Coal.	Penna. Pittsburg.	W. Virginia. Fairmont.	Kentucky. Straight Creek.	Ohio. Hocking Valley.	Ind. Ter. Hartshorn.
Moisture	1.07	1.35	1.92	6.72	3.87
Volatile matter	39.24	36.92	36.56	37.13	35.73
Fixed carbon	50.92	55.36	57.08	50.32	50.05
Ash	8.77	6.37	4.44	5.83	10.35
Carbon	82.47	78.31	78.31	69.42	69.85
Hydrogen	6.01	5.26	5.36	5.35	5.14
Oxygen	6.81	7.61	8.80	16.27	11.38
Nitrogen	1.88	1.55	1.85	1.46	1.29
Sulphur	2.83	.90	1.24	1.67	1.99
Heating value, B.T.U. per pound	15353	14164	14319	12388	12620

The result of distilling coal at various temperatures has been quite carefully studied by a number of observers, and it has been found that not only the percentage of the volatile matter, but its composition plays an important part.

It is notable that some of the newer Western coals yield considerably less gas than the Eastern coals having the same content of volatile matter. The ultimate analysis of a coal does not throw very much light on its suitability for the manufacture of gas, although certain general indications may be derived from it. In general, increasing percentages of hydrogen result in more volatile constituents, and high percentage of oxygen apparently decreases the yield of gas and slightly increases the yield of tar. The higher percentages of nitrogen usually result in more ammonia. The presence of sulphur is to be avoided as far as possible, yet its manner of occurrence is important in determining whether it will be volatile and go off in the gas and have to be removed, or whether it will remain in the coke. Where the coke is to be used for the manufacture of water gas, the composition and fusing point of the ash is important, while in case it is to be used for foundry work, the absence of sulphur and phosphorus is essential.

Chemical Theory of Coal Carbonization. The carbonization of the coal proceeds in three general stages:

First. There is a preliminary decomposition, which begins as soon as the coal has reached a temperature of from 650°–750° F., and as this stage is quite strongly endothermic, approaching as it does a fusion, the temperature remains practically constant until completion.

Second. The products resulting from the first stage, which consist principally of the higher members of the aliphatic series suffer molecular rearrangement with the formation of compounds containing probably less than three atoms of carbon. The first two stages take place almost simultaneously within the charge itself.

Third. The gaseous vapors resulting from the second stage when evolved from the protecting influence of the coal particles are acted upon by the conducted and radiant heat of the more highly heated portions of the charge proper, of the sides of the containing retort and of the highly heated surfaces with which the vapors may come into contact.

The reactions that take place during the third stage are very complicated and depend upon the temperature, time of contact and pressure. The influence of these factors are so intermingled that it is difficult to give each its true value as affecting the whole.

There results from the distillation of coal three classes of products: gases—condensed watery solutions—condensible hydrocarbons and a carbonaceous residue.

These products are known commercially as coal gas—ammoniacal liquor—coal tar and coke. The average distribution of the elements in the coal into these products with their analysis is given in the tables below:

COMPOSITION OF COKE

	German.	English.	French.	American.
Carbon	84.76	90.75	84.35	81.34
Hydrogen	.90	.45	.67	.57
Oxygen	.34	1.50	1.35	2.40
Nitrogen	1.38	1.20	.40	.89
Sulphur	.93	.60	1.06	1.04
Ash	9.42	5.50	12.17	13.76
Moisture	2.27			

ELEMENTARY COMPOSITION OF COAL GAS

	Horizontal.	Vertical.	Coke Ovens.	French Hor.	English Hor.
Carbon	53.67	51.77	51.95	57.09	58.62
Hydrogen	21.04	20.86	19.15	19.45	22.37
Oxygen	16.43	17.56	13.05	19.65	15.34
Nitrogen	8.92	9.81	15.83	3.81	3.65

COMPOSITION OF COAL TAR

	Average.	Hydraulic.	Scrubber.	Condenser.	Holder.
Carbon	84.91	90.186	89.91	87.222	85.183
Hydrogen	9.65	4.848	4 945	5.499	5.599
Oxygen	3.50	4.966	6.279	6.279	9.218
Nitrogen	1.60				
Sulphur	.34				

DISTRIBUTION OF COMPONENTS OF COAL BY DISTILLATION

	Coal.	Coke.	Tar.	Gas.	Liquor.
Ash	8.18	8.18			
Moisture	4.34	.....	.....	.....	4.340
Carbon	72.08	56.453	5.418	10.209	
Hydrogen	4.78	.446	.378	3.481	.475
Oxygen	8.73	.909	.504	3.516	3.800
Nitrogen	.87	.271	.042	.374	.183
Sulphur	1.02	.712		.308	.....
Totals	100.00	67.071	6.342	17.888	8.799

GENERAL DISTRIBUTION OF PRODUCTS

From 100 lbs. of Coal

System.	Horizontal.	Vertical.	Coke Ovens.	Munich Chambers.
Coal.	Yough.	Westphal.	Dominion.	Saar.
Volatiles	34.8%	26.1%	34.6%	31.2%
Coke	68.6 lbs.	71.0 lbs.	71.13 lbs.	67.88 lbs.
Gas	18.4	16.3	16.43	15.60
Tar	7.8	4.58	3.38	6.19
Ammonia,	.229	.326	.34	.239

If we should express the ultimate composition of these products as complex molecules the decomposition of the coal might be represented by the following equation:

$$\underset{\text{Coal.}}{C_{357}H_{281}O_{29}} = \underset{\text{Coke.}}{C_{280}H_{26}O_8} + \underset{\text{Tar.}}{C_{27}H_{22}O_2} + 5\underset{\text{Gas.}}{C_{10}H_{41}O_3} + 14\underset{\text{Water.}}{H_2O}.$$

If the heats of combustion are calculated by the Dulong formula it will be found that the sum of the heats of combustion of the products is less by some 2.42 per cent than the heat of combustion of the coal, so that the reaction is exothermic by about 339 B.T.U. per pound of coal, which represents the heat liberated and thus lost during the distillation.

The relative occurrence of the constituents of these products is in general dependent upon the complex reactions that take place in the third stage of the carbonization. As at the temperature of their formation these products are evolved as vapors we may consider them together and later discuss the different products formed by condensation.

The theory of the formation and molecular rearrangement of the various hydrocarbons under the influence of heat has been studied by a number of experimenters. The early theory propounded by Berthelot assumed that acetylene was the primary product of the pyrodecomposition and that all the products were the result of its condensation. Many other workers enlarged this idea, but from the more recent work

we do not look for the primary formation of acetylene but rather expect a splitting off of the terminal hydrogen and carbon atoms with the formation of residues such as $H_2C=$ and $HC\equiv$ which according to the temperature and other conditions may combine with each other: take up hydrogen or decompose into their elements.

A very large amount of work has been done recently on the composition of coal, principally with the use of various organic solvents. In this manner two main fractions can be separated, the one probably related to the original cellulose and the other to the resinous constituents in the coal. These complex organic materials seem to correspond closely to the light tars or oils produced by the distillation of the coal at low temperatures and in a vacuum. They usually show a very large percentage of phenolic bodies together with a trace of aromatic hydrocarbons. When these oils are subjected to temperatures ranging from 550 to 800° C. there is a progressive decomposition of the olefines and higher paraffines and naphthenes and an increasing production of aromatic hydrocarbons.

There has been a tendency to ascribe to the naphthenes an important part as intermediate products in these secondary transformations, but it appears more likely in view of our present knowledge that probably the higher members of the olefine series are of great importance, in view of the fact that the naphthenes appear to break down at somewhat lower temperatures than those at which practice indicates the maximum formation of aromatic hydrocarbons taking place. In view of the very considerable amount of work that has been done on this problem especially in connection with thermal decomposition of paraffine hydrocarbons and probable course of rearrangement may be as follows:

The table below gives the general direction of the pyrocondensations at the lower and higher temperatures. It assumes that the simpler olefines and paraffines are the result of the first two stages of the carbonization and shows the probable products due to the influence of the higher temperatures that are effective during the third stage.

PROBABLE COURSE OF REARRANGEMENT OF HYDROCARBONS

Primary Products: Ethylene, methane, ethane and possibly hydrogen.

Ethylene → ethane+methane+hydrogen.
Ethane → acetylene+ methane+hydrogen.
Acetylene → benzol.
Benzol → diphenyl, anthracene, phenathene.
Benzol+acetylene → napthalene.
Benzol+ethylene → styrolene and other tarry products.
Styrolene+benzol → napthalene diphenyl. Acetnaphthalene, anthracene, and phenanthrene.

While the results given in the above table are from experimental data the tables below will give the results of actual conditions in carbonizing as affecting the composition of the gas, tar and coke at different periods of the distillation and under different temperature conditions.

The effect of the proper and regulated amount of superheating is well shown by the superior results obtained with the American type of vertical retorts which are not completely filled and the upper 4–5 ft. of the retort acts as a fixing chamber as against the German type in which the retort is completely filled and no fixing surface exists.

It will be noted that as the temperature rises and the time of exposure increases (due to the small make of gas) the change and the character of the products closely follows the directions that the experimental investigations have predicted. The gradual decrease in the olefines and ethane and the increase in the methane and hydrogen. It must be remembered in studying these results that the doubling of the volume of hydrogen as it is given off tends to mask the volumetric relations of the other hydrocarbons whose volume is not doubled and in some cases results in a contraction of volume.

RESULTS OF DIFFERENT CARBONIZING TEMPERATURES

Temperature	800° F.	1000° F.	1200° F.	1400° F.
Yield, cubic feet per pound	.409	1.233	2.319	3.601
Candle power	.....	19.7	18.9	16.0
Candle feet	.....	24.29	43.38	57.6
B.T.U.	523	651	745	626
Tar, gallons per ton	12.6	23.8	22.4	28.6
Coke, per cent	78.8	69.5	67.8	66.95
Volatiles in coke	22.04	13.00	7.97	5.88
Ammonia, pounds per ton	.37	1.47	2.29	3.71
Ills	6.00	5.85	5.75	4.50
CO	4.00	4.90	4.70	7.30
H_2	19.66	22.03	32.13	39.70
CH_4	18.45	30.78	36.53	37.30
C_2H_6	8.02	7.84	8.27	1.60
CO_2	7.80	6.00	3.45	3.20
O_2	.60	.30	1.20	1.35
N_2	35.47	23.23	7.97	5.05

The pressure at which these reactions take place has a considerable influence on the products formed. Owing to the permeability of the retorts if too low a pressure is maintained furnace gases will be drawn in, which would seriously lower the candle-power, while on the other hand an excessive pressure, by retarding the evolution of the gas, tends to result in excessive decomposition and in the formation of graphitic carbon. Experience points generally to a balanced pressure just equal to that of the atmosphere, and it should be maintained as nearly constant as possible. This latter condition is probably best insured by the use of retort house governors.

It will be noted from the foregoing that the gas obtained from a pound of coal and its illuminating value depends upon a number of factors, viz., the coal, the system of carbonization employed, the temperature in the

VARIATIONS DURING DISTILLATION

Vertical Retorts

Hours after Charging	1st	2d	3d	4th	5th	6th	7th	8th	9th
	%	%	%	%	%	%	%	%	%
Proportion of yield	16.8	14.1	13.0	11.9	11.7	11.2	9.6	6.5	5.2
Candle power	20.7	20.2	19.5	17.9	15.0	12.9	8.1	1.9	
Heating Value in B.T.U.	701	765	707	678	625	597	542	446	400
Ammonia, grains per 100 cu.ft.	540	440	380	250	250	250	130	70	40
H_2S, grains per 100 cu.ft.	510	470	430	295	285	260	180	100	50
Ills	8.05	8.00	7.70	5.60	4.10	3.60	2.80	.80	.30
CO	8.90	7.20	8.40	8.60	7.05	8.60	7.70	7.60	6.30
H_2	38.25	37.80	36.80	39.00	44.15	45.80	57.40	66.90	68.80
CH_4	38.45	39.60	41.30	42.00	39.60	37.40	27.00	20.70	18.60
C_2H_6	3.00	2.70	1.70	1.30					
CO_2	1.95	2.85	2.40	2.20	1.95	2.50	1.80	1.90	2.70
O_2	.40	.20	.20	.15	.55	.20	.30	.30	.80
N_2	1.00	1.65	1.50	1.15	2.60	1.90	2.00	1.80	2.50

retorts, and several other conditions. It is interesting to note that for any given coal, that the product of the yield of gas per pound in cubic feet and the candle-power, i.e., the candle-feet, is quite constant, its value for different coals varying from 65 to 80. Assuming an average candle-power of 14 this results in yields of from 4.65 to 5.75. Some of the Western coals will rarely yield over 4.5 cu.ft. per pound while nearly all the better Eastern coals will yield over 5.00 cu.ft. under proper operating conditions.

In addition to the other gases which have been considered, there are present ammonia, cyanogen, hydrogen sulphide, carbon disulphide and traces of some other organic sulphur compounds that need not be considered. The ammonia and hydrogen sulphide both appear early in the distillation, soon reach their maximum and then decline, the ammonia somewhat faster than the hydrogen sulphide. The cyanogen and carbon disulphide on the other hand gradually increase as the temperature rises.

There seems to be some connection between the proportion of ammonia and cyanogen which has been explained by the probable reaction:

$$NH_3 \begin{cases} 2CN + 3H_2 \\ N_2 + 3H_2 \end{cases}$$

The critical temperatures of maximum yield seem to be about 850–900° F. for ammonia and from 1650–1750° F. for cyanogen. When the temperature rises above 1800° F. these gases seem to be decomposed into their elements.

The yield of ammonia and cyanogen is naturally dependent upon the amount of nitrogen present in the coal, but is apparently more affected by the system of carbonization. Generally with the higher temperatures

the yield of ammonia is decreased while the cyanogen increases, but this is not always the case, the ammonia and cyanogen sometimes varying in the same direction. It will be noted from the following table that the horizontal retorts yield less ammonia than either the vertical retorts or the coke ovens.

	Horizontal.	Vertical.	Coke Ovens.
Nitrogen in Coal	1.25%	1.31%	1.29%
Ammonia, as NH_3 per ton	4.5#	6.1#	6.8#
Cyanogen, as CN per ton	2.4#	1.2#	1.5#

The ratio and quantity of hydrogen sulphide and carbon disulphide seems to vary not only with the temperature but also with the method of carbonization as the vertical retorts apparently yield less fixed sulphur compounds than the horizontal retorts and probably more hydrogen sulphide. In general the total sulphur compounds in the gas increase with the sulphur in the coal, but a table below shows how the sulphur is distributed with some American coals when tested in horizontal retorts.

RELATION OF SULPHUR IN COAL AND COKE TO HYDROGEN SULPHIDE AND SULPHUR COMPOUNDS

Coal.	Sulphur in Coal.	Sulphur in Coke.	Grains per 100 Cu. Ft.	
			Hydrogen Sulphide in Gas.	Sulphur Compounds.
Equality	6.76%	2.27%	2190	45.51
Marian	2.39	2.38	955	30.00
Montana	1.64	1.53	735	45.30
Cartersville	1.59	1.28	910	40.45
Gaston	1.35	1.15	702	65.23
Big Muddy	1.21	.82	340	17.42
Youghiogheny	1.01	.93	420	17.28
Farmington	.96	.84	400	18.64
McAllister	.94	.66	260	12.00

Coal Tar. In addition to the gaseous hydrocarbons formed during the third stage of the carbonization the very complex mixture of ring hydrocarbons and their derivatives having boiling-points considerably above that of water are formed and condensed into what is known as tar. The table on page 495 gives a comparison of the distillation of a number of samples from the different methods of carbonization.

This shows the variation in the character of the hydrocarbons that are formed with the increasing time of distillation and increase in temperature. The increasing gravity and the higher fixed carbon content denote the increasing complexity of the hydrocarbons formed.

The yield of tar varies with the coal and other carbonizing conditions. It generally decreases with higher temperatures and an increased

	Water Gas Tar.	Continuous Verticals.	Intermittent Verticals.	Chamber Ovens.	Coke Ovens.	Horizontal.
Specific gravity	1.081	1.079	1.123	1.122	1.155	1.226
Free carbon...	.32%	3.4%	3.2%	5.4%	8.0%	23.03
Unsulphonated	1.98%	12.5%	10.1%	6.1%	4.3%	2.1%
Coke.....	23.1%	18.7%	22.7%	24.6%	33.5%	52.67

Distillation	%	Sp. Gr.	%	Sp. Gr.	%	Sp. Gr.	%	Sp. Gr.	%	Sp. Gr.	%	Sp. Gr.
Start –250	.0	.....	2.5	.905	.0	.....	.0	.....	.0	.....	2.6	.961
250–300	.0	.....	1.5	.920	2.0	.921	2.0	.898	.0	.....	.....	.....
300–350	4.0	.907	4.5	.925	1.3	.933	4.0	.904	.0	.....	.2	.....
350–400	5.4	.929	9.7	.963	7.0	.979	5.5	.971	.0	.....	2.0	1.004
400–450	5.3	.974	13.5	.993	11.0	1.008	13.5	1.018	9.0	1.041	6.9	1.029
450–500	11.9	1.004	11.5	1.022	7.0	1.030	10.0	1.025	10.0	1.080	11.4	1.039
500–550	.82	1.017	11.5	1.055	6.8	1.050	3.8	1.055	3.4	1.098	5.7	1.064
550–600	13.7	1.038	20.0	1.095	8.1	1.081	6.0	1.079	4.8	1.102	5.1	1.117
600–650	13.0	1.091	8.0	1.189	13.3	1.113	9.3	1.104	9.0	1.120	7.5	1.132
650–700	8.5	1.123	....	.....	22.0	1.156	9.4	1.135	10.2	1.187	1.7	1.158
700–750	8.0	1.176	....	.....	....	.....	9.2	1.165	9.5	1.192	4.4	1.185
Above 750	....	.....	....	.....	....	.....	3.1	1.225	10.2	1.200		

yield of gas. With horizontal retorts the tar yield may vary from 10 to 14 gallons per ton, with vertical retorts from 12 to 16 gallons, while from coke ovens the yield may be as low as 5 to 8 gallons.

The utilization of coal tar has given rise to an industry that is increasing in importance with great rapidity, especially during the last three years, and it is not too much to expect that, given an abundant supply of crudes, i.e., benzol, toluol, naphthalene, etc., that with further working up of these products into the finer organic chemicals, dies and synthetic drugs the United States will be in a position to seriously challenge the present position of Germany and England in this industry.

Coke. The coke or carbonaceous residue that remains in the retort is influenced by the methods and temperatures employed in the distillation. The coke produced in the ordinary retorts where the charge of coal is small, the time short and temperature rather low, is porous, soft, and contains several per cent of volatile material. As the size of the charge increases and the time is lengthened the coke loses the volatile matter, becomes harder and more metallic in appearance and is stronger and denser, so that it becomes available for foundry purposes. In the coke oven, Fig. 205, where the charge is still larger and the time extends to 24 hours, or in the bee-hive ovens to 48 hours, the most valuable grades of coke for iron and steel industry are produced. The dense character is dependent apparently upon the length of time the coke is acted upon by the heat and upon the weight of the charge which causes a compression within itself.

The percentage of fixed carbon in the coal practically fixes the percentage of coke yield, yet this is affected slightly by the system of carbonizing. The vertical retorts yielding a slightly higher percentage

than the horizontal retorts while with the coke ovens there is a considerable increase; in this case, however, the increased yield of coke seems to be at the expense of the tar.

The table, on page 495, of analyses of the coke from the different processes shows clearly the above variation in physical characteristics.

COMPARATIVE COKE ANALYSES

	Bee-Hive Ovens.	Retort Coke Ovens.	Vertical Retort.	Horizontal Retort.
Moisture	.35	1.25	1.35	2.57
Volatile compounds	.34	1.61	1.73	3.84
Fixed carbon	92.69	86.66	87.40	86.05
Ash	5.89	10.48	9.52	7.54
Sulphur	.74	.77	.99	.96
Real gravity	1.83	1.90	1.82	1.73
Per cent of coke	52.07	49.49	59.25	53.89
Per cent of cells	47.93	50.51	40.75	46.11

Gas. The gas as it issues from the coal passes out through the mouth-piece and up the ascension pipe, and by means of the dip-pipe enters the hydraulic main. This acts as a seal to prevent the gas escaping from the hydraulic main back into the retort when the mouth-piece is open for charging or discharging. Fig. 209 shows the general plan of coal gas plant.

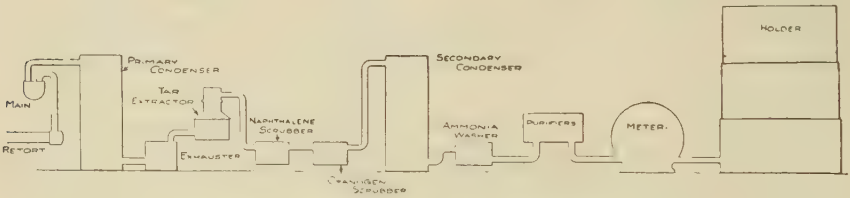


FIG. 209.—Outline of Condensation and Purification of Coal Gas.

Ordinarily, there is an ascension pipe for each retort, but in some cases one ascension pipe serves three retorts, which are set directly above one another. This system is, of course, only applicable where the retorts are charged and discharged simultaneously by machinery.

Hydraulic Main. The desirability of the use of a liquid seal in the hydraulic main is subject to some question, and there are a number of methods proposed and in use whereby this seal may be lowered after the retort has been charged, thus putting the retort in direct connection with the hydraulic main, and then raising it so that the retort is sealed off when the lids are opened for charging and discharging. Valves of different design have also been used for this purpose.

When the hot gases come in contact with the liquid in the hydraulic main, a certain amount of tar is deposited; this is removed automatically

from the main in order that it may not come into direct contact with the gas, and thus cause a deterioration of the candle-power.

The crude gas leaves the hydraulic main at a temperature of from 130°–150° F., and contains a number of impurities—tar, ammonia sulphuretted hydrogen, organic sulphur compounds, naphthalene and cyanogen—which must be removed in whole or in part before the gas is considered ready for distribution, and, furthermore, the gas must be brought down to the ordinary temperature. The average content of the impurities in the crude coal gas is given below.

IMPURITIES IN CRUDE COAL GAS

Impurity.	Percentage by Volume.	Grains per 100 Cu.Ft.
Hydrogen sulphide	.4 –1.6	250–1000 sometimes 3000
Ammonia	.48 –1.26	150–400 occasionally 550
Cyanogen	.05 – .135	25–65
Organic sulphur	.0085– .046	12–65

Condensers. When the gas leaves the hydraulic main it contains in addition to the impurities just mentioned a very complex mixture of hydrocarbons of widely varying boiling points, in addition to the water vapor with which it is practically saturated. Some of the hydrocarbons are fixed gases at the ordinary temperatures while the others may be vapors, liquids or solids; while practically all are mutually soluble in each other and to some extent in water. As much of the illuminating value of the gas is due to the vapors of the benzol homologues it is important that these be retained in the gas as far as possible, while on the other hand the heavier hydrocarbons, especially napthalene, must be removed as far as possible on account of their interference with succeeding stages of the purifying process or with the distribution of the gas itself.

As the gas must be reduced in temperature for the succeeding stages in the purifying process the reduction forms a convenient method of removing the heavier hydrocarbons which condense, forming a dark viscous liquid known as tar. Owing to the mutual solubility of the components of the tar it is of the utmost importance that the conditions under which the gas is cooled be carefully regulated, as depending upon this regulation, the valuable illuminating hydrocarbons will remain permanently in the gas; remain until the gas is purified and then condense in the street mains, or drop out of the gas in the condensers and appear in the tar. The complete removal of the tar and the temperature at which this takes place are therefore of importance as affecting the illuminating value of the gas.

At the temperature at which the gas leaves the hydraulic main, the tar exists principally as a fog, and also as a vapor which will condense with a lowering of the temperature. This is effected in the primary

condensers, one form of which is illustrated in Fig. 210. The cooling agent may be either water or air. In a recent system the cooling water

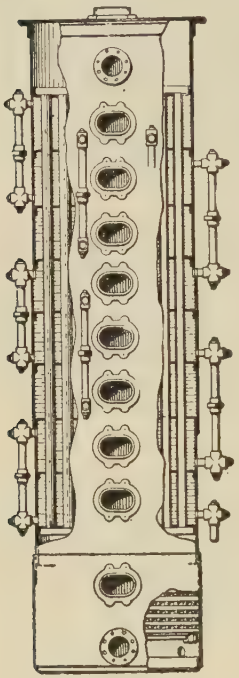


Fig. 210.—Dephlegmating Condenser.

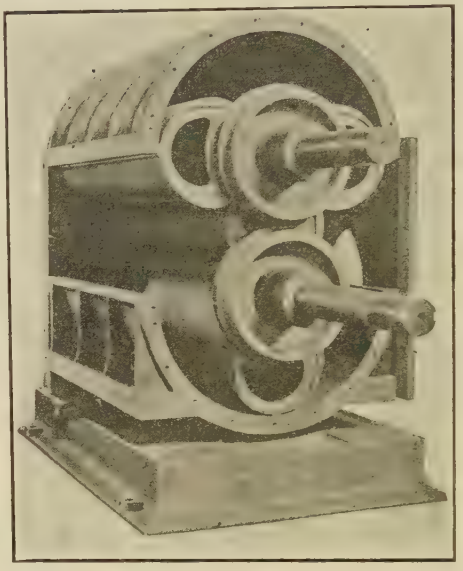


Fig. 211.—Exhauster.

is sprayed through the gas assisting in the removal of the tar, and the water is then freed from tar, cooled and recirculated.

Tar Extractor. On leaving the primary condensers, in which some of the tar is deposited, the gas is passed into some form of tar extractor, the usual form being that of the P. & A., which consists, as shown in Fig. 212, of a drum composed of a series of perforated sheets consisting of alternate series of small holes and blanks so arranged that the blank spaces in one set of sheets opposes the perforated sections in the adjoining sheets. Another form of apparatus

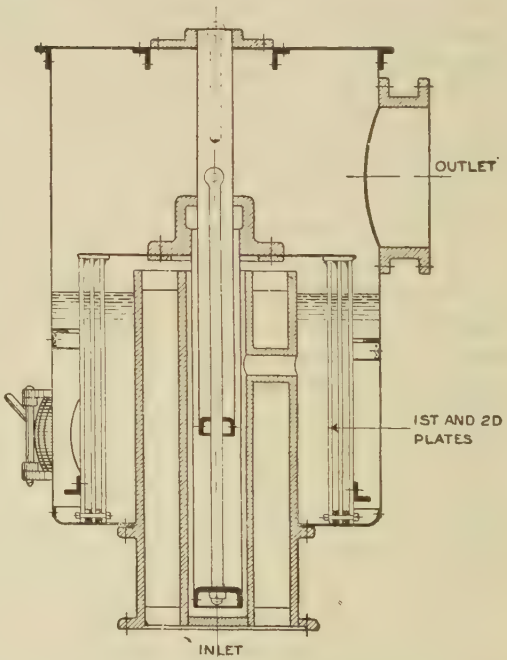


Fig. 212.—F. & A. Tar Extractor.

is known as the washer-scrubber. In this, the gas passes through a number of small openings into contact with ammonia liquor, the action of the water causing the tar particles to coalesce and be condensed. It is found that the most efficient operation for the removal of tar requires a temperature of from 105° to 115° F.

Exhauster. The gas is now passed through the exhauster, Fig. 211, which operates to maintain a constant pressure in the retorts and to furnish the pressure necessary to overcome the resistance of the train of purifying apparatus, and to force the gas into the storage holder.

Scrubber. From the exhauster the gas passes into the one or more of a series of scrubbers for the removal of naphthalene, cyanogen and ammonia. Four general types are in use, tower, static, rotary and centrifugal.

The tower scrubber was the original form and consists of one or more steel towers filled with various materials, to break up the upward stream of gas and to increase the surface covered with the scrubbing liquid that is sprayed in at the top and passes downward by gravity. Coke quartz, various forms of wooden trays, boards set on edge, etc., have been used for this purpose. This type of scrubber is the least efficient considering its cubical capacity but is fairly efficient if built quite high per square foot of ground space required. In the static type the gas is forced to pass in contact and bubble through the scrubbing liquid by a series of partitions arranged across the flow of gas in a rectangular containing vessel. Another series of divisions permits the level of the scrubbing liquid to be regulated in the various compartments thus formed so that the most efficient depth of seal may be maintained.

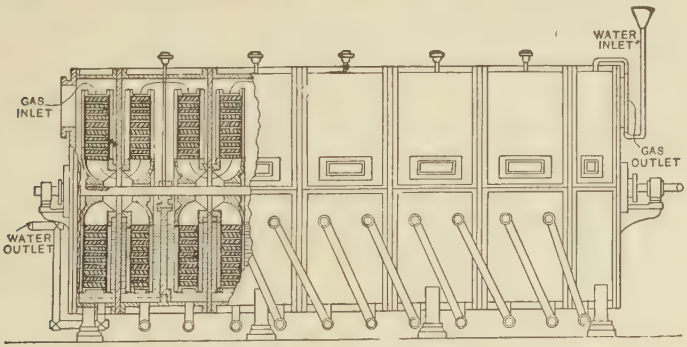


FIG. 213.—Rotary Ammonia or Naphthalene Scrubber.

Fig. 213 is a sectional elevation of the rotary or mechanical type of scrubber.

These are composed of horizontal cylinders divided by a number of vertical partitions. A central shaft carries a disk made up of a large number of short wooden rods set parallel to the axis of the shaft, and arranged so that as they revolve they dip into the contents of the scrubber,

and on rising present a large wetted surface in contact with the stream of gas.

The centrifugal type of scrubber is of more recent development. Fig. 214 is a Feld type. In these the scrubbing liquid in descending from one compartment to another is thrown into a sheet of spray by the action of the revolving cones attached to the central shaft. The gas is forced to pass through this spray a number of times in rising through the apparatus.

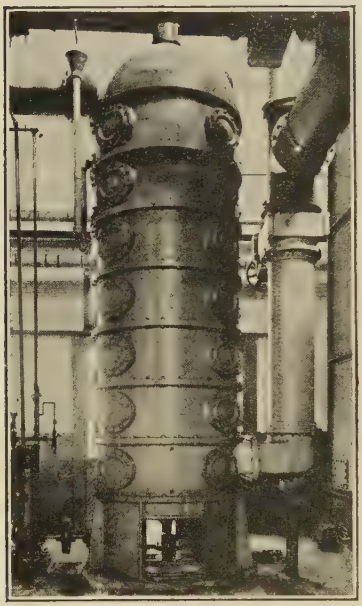


Fig. 214.—Feld Centrifugal Scrubber.

For the removal of naphthalene the tower, static, or rotary scrubbers are used, and tar oil, gas oil, or water gas tar is used as the scrubbing liquid.

In the removal of cyanogen either the rotary or centrifugal scrubber is employed.

The solutions used vary according to the processes employed, but they usually consist of an alkaline solution of ferrous sulphate. The gas now passes to the ammonia scrubbers, Fig. 213. In order that the absorption of ammonia by water, which is usually used to remove it, will be complete, it is necessary that the temperature of the gas be reduced to about 60° F. This reduction in temperature is secured in the secondary condensers; these are always water cooled in order to secure the low final temperature that is necessary.

This absorption was formerly carried on in large towers filled with cobble stones or boards, or other devices exposing a large surface, which was kept moistened by water or weak liquor passing down from the top. This form of scrubber has been generally replaced by the more compact rotary or centrifugal scrubbers. In these mechanical scrubbers the ammonia is completely removed by the use of from 10 to 15 gallons of water per ton of coal carbonized, and as the gas is at the same time brought into contact

REMOVAL OF IMPURITIES IN CRUDE COAL GAS BY CONDENSATION AND SCRUBBING

	Hydrogen Sulphide Grains per 100 Cu.Ft.	Ammonia. Grains per 100 Cu.Ft.	Carbon Dioxide. Per Cent by Volume.
Outlet of exhauster	610	223.1	2.57
Outlet of condensers	590	196.4	2.34
Outlet of tower scrubbers	470	93.1	1.98
Outlet of rotary scrubbers	400	.37	1.58

with the concentrated ammonia liquor at the inlet end of the scrubber, a considerable proportion of sulphuretted hydrogen and carbon dioxide is also removed.

Recently the use of ammoniacal liquor, which has been freed from the greater part of its sulphuretted hydrogen and carbon dioxide by heating in the presence of ammonia gas as a scrubbing liquid has resulted in the removal of approximately half of the hydrogen sulphide and a considerable proportion of the carbon dioxide.

Ammonia Liquor. The ammonia liquor and tar that are removed in the different points in the condensing and purifying system are collected and passed through what is known as a separator. In this apparatus, the stream of mixed liquor in passing through the separator is baffled and turned in its course a number of times, so that the tar which has a specific gravity of 1.2, and higher, falls to the bottom and may be removed, while the liquor rises to the top and may be pumped off to the ammonia storage tanks. See Fig. 215.

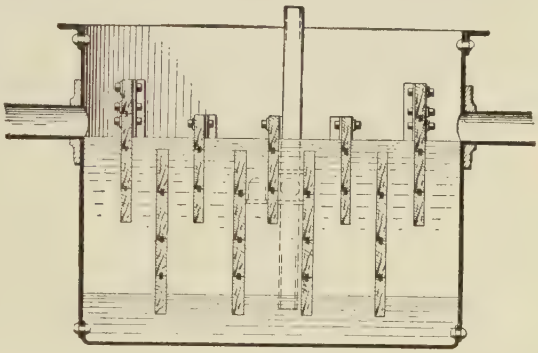


Fig. 215.—Tar Separator.

A number of processes have been invented for the extraction of the ammonia from the heated gases and the direct formation of ammonium sulphate; among these are the Otto, Collin, Koppers, and Feld.

In the Otto the gases are cooled with air to a temperature of 200° F. and then with a tar spray to about 160° F. The spraying with tar which takes place in two stages is utilized to remove the greater portion of the tar vapors, the gas is then scrubbed with a modified P. & A. extractor and is then passed into the lead-lined saturator, where it comes in contact with sulphuric acid heated to 165° F. This is necessary to prevent the deposition of the water vapor carried in the gas, after leaving the saturator, the gas passes through a baffle chamber to remove acid spray.

In the Collin process the gas, after passing through the usual condensers and P. & A. extractor, is cooled to about 75° F. and then passes to the upper of two saturators, where the acid is kept in excess. The overflow from the upper saturator passes to the lower saturator into which is passed the ammonia gas driven off from the liquor condenser in the preliminary water cooler. One of the objects obtained in this system is the elimination of certain amount of H_2S, HCN, etc., that are combined with the ammonia liquor, as the exit gases from the second saturator pass directly to the air.

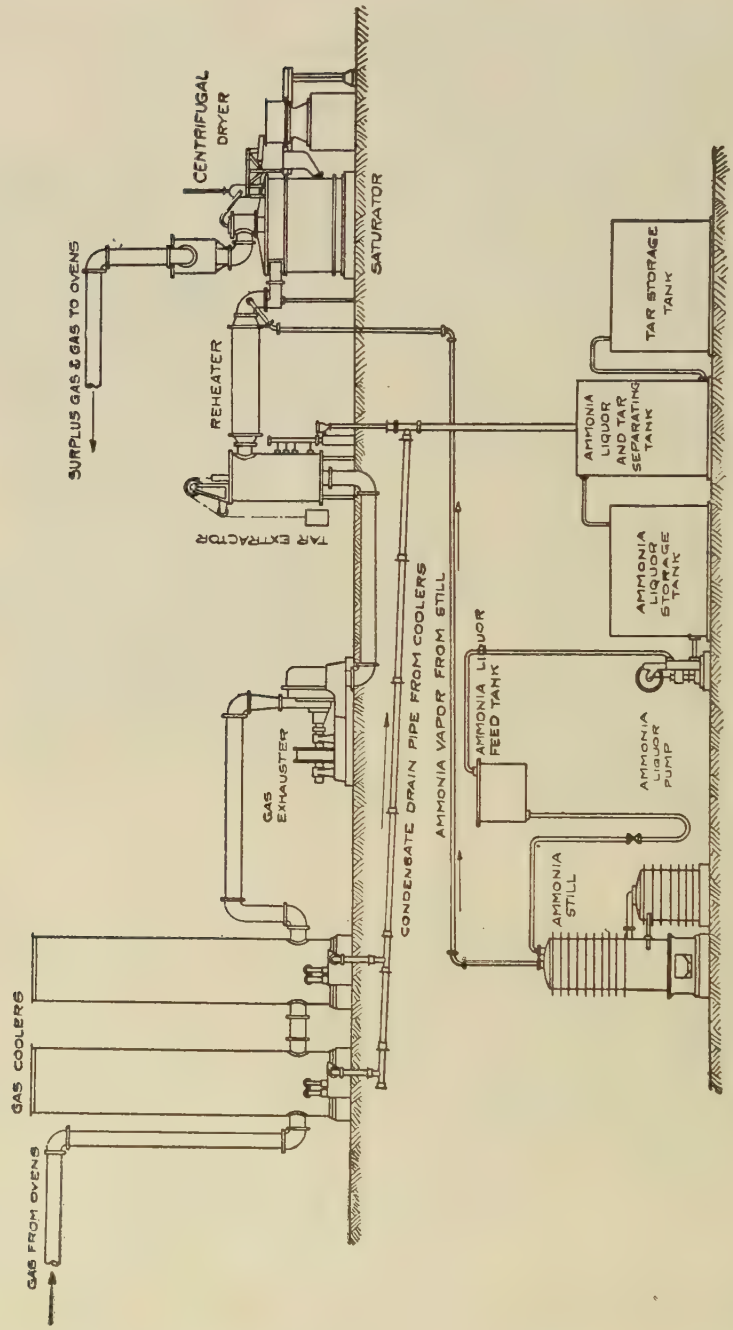


FIG. 216.—Outline of Koppers System of Direct Ammonia Recovery.

In the Koppers system which is quite extensively used in this country, the gas is gradually cooled to about 225° F.; with air and water cooler condensers it is then passed through a P. & A. tar extractor to remove the

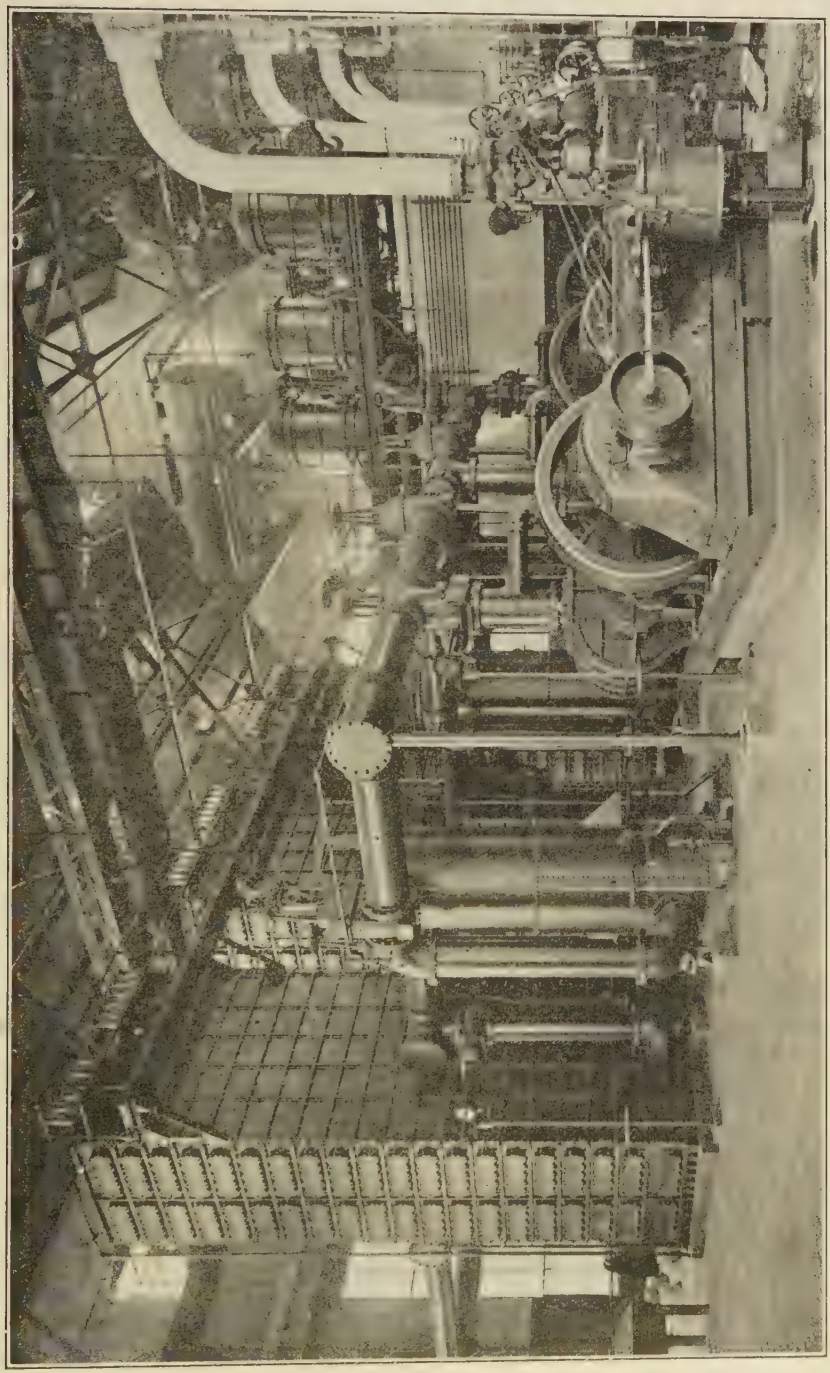


Fig. 217.—Installation of Koppers Ammonium Sulphate Plant.

tar and is then heated with exhaust steam to about 176° F. at which temperature it passes to the saturators. The ammonia liquor condensed

in the cooler is driven off in a small still and added to the gas just before it enters the saturators. An outline of this system is given in Fig. 216, and the view of a large installation is given in Fig. 217. The saturators are provided with siphon devices thereby the ammonium sulphate is driven out of the bottom saturator and delivered into the centrifugal machine where it is freed from moisture.

In the Feld system the gases after passing through the condensers and tar extractors are washed with a solution of ammonium polythionate which absorbs the ammonia from the gases, forming ammonium thiosulphate and precipitating free sulphur. This solution is treated with sulphur dioxide, which regenerates the polythionate, and precipitated sulphur is removed. In order to recover the ammonium sulphate, the polythionate solution is heated with exhaust steam to 150–160° F., at which temperature it is decomposed to ammonium sulphate, free sulphur and SO_2. The SO_2 is used in the earlier stage in the process. The sulphur is filtered off, the ammonium sulphate solution evaporated to crystallization. The Feld system has not been adopted to any considerable extent as yet.

The remaining impurities in the gas are sulphuretted hydrogen and organic sulphur compounds.

Purifiers. The sulphuretted hydrogen is generally removed by passing it through large vessels, called purifiers, Figs. 218 and 219, where it is

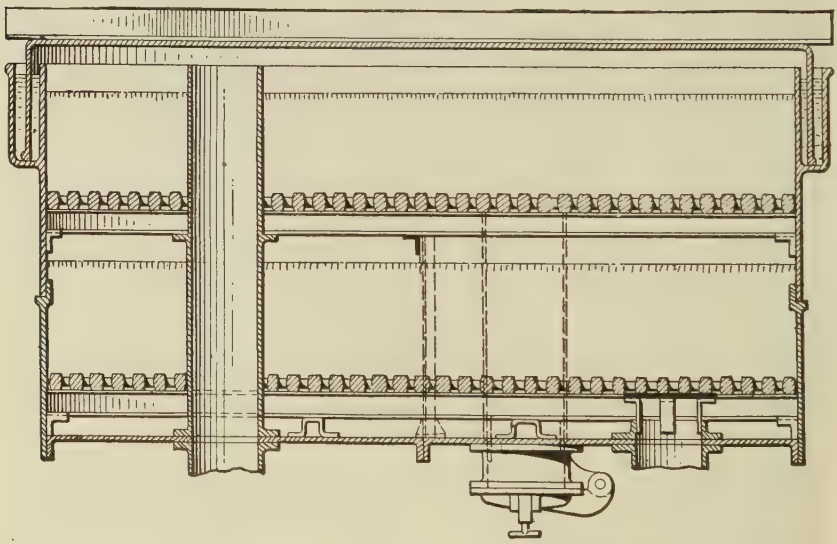


Fig. 218.—Water-sealed Purifier, Shallow Type.

brought into contact with some form of ferric oxide. There is considerable discussion as to the exact reactions which take place. The probable reactions are

$$Fe_2O_3+3H_2S=Fe_2S_3+3H_2O$$

and

$$Fe_2O_3+3H_2S=2FeS+S+3H_2O.$$

It seems likely that these two reactions take place simultaneously, and the proportions of ferric and ferrous sulphide formed are dependent upon the nature of the oxide and the other conditions. It is said to be in the relation of three parts ferric to five parts ferrous sulphide. When the oxide has become saturated it is removed from the purifiers and exposed

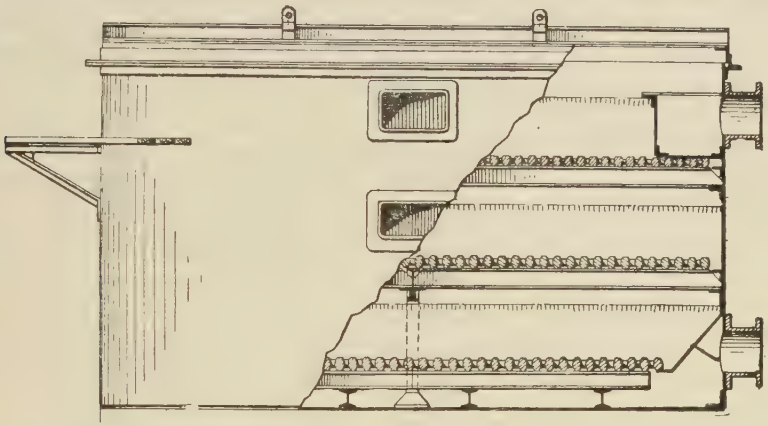


Fig. 219.—Dry-seal Purifier. Deep Cheese-box Type.

to the air, where, under the influence of the atmospheric oxygen, ferric oxide is formed and free sulphur set free.

In order to take advantage of this reaction, small quantities of air are sometimes admitted to the crude gas before entering the purifiers, the oxygen in which reacts with the partially fouled purifying material, and thus considerably increases the length of time before it is necessary to remove it.

In some plants the oxide is revivified while in place by circulating through the box, air or gas mixture containing at first a very small percentage of free oxygen, the heat given off in the revivification is removed by cooling usually with a water spray so that the purifier is thoroughly saturated with water vapor as the revivification proceeds the amount of oxygen is allowed to increase. In this manner under very careful operating control it is possible to increase the sulphur in the oxide up to 40 per cent without removing it from the purifying vessel. With certain classes of oxide it is exceedingly difficult to carry this out without danger of local superheating taking place resulting rise in temperature of the oxide to such a point that the oxide is destroyed or when the box is again put in service carbon bisulphide compounds present in the gas are changed into sulphuretted hydrogen.

The purifying material is composed of either a natural ferric oxide or, as is generally the case, made by coating shavings, planer chips or corn cobs with some form of ferric oxide.

The efficiency of the purifying material thus made seems to depend

upon the nature of the ferric oxide; the more active oxides are apparently colloidal in nature. Where the oxide is made by rusting iron borings on the chips the organic acids in the wood act as protective colloids and result in the formation of varying percentages of the iron in the colloidal form.

Certain natural oxides and some of the artificial oxides that result as by-products in the manufacture of alums are found to have a considerable proportion of their iron content in the form of a hydrogel of ferric hydroxide. Apparently it is the enormous surface that is presented by these collodial oxides that explains the increased chemical efficiency of oxides in this state. .

In the older type of purifiers the oxide was contained in shallow cast-iron boxes provided with water sealed lids, the oxide being carried on wooden trays in two layers of about 30 ins. each. These boxes were arranged usually in sets of four or six, and so connected with valves that the sequence of boxes could be varied at will, and any box could be removed from service for cleaning.

It has now been found more economical to put the oxide into only two or three large boxes, building these either of steel or concrete out of doors, and thus saving expensive buildings.

Widely divergent views are held as to whether it is the time of contact, the velocity of flow, or the total volume of the oxide in use that is the determining factor in calculating the apparatus necessary for the purification of the gas. It is usually estimated, however, that with the use of a slow velocity a certain total volume of purifying material is required.

The economical volume of oxide and its uses are functions of the capital charges for installation and the cost of changing and revivifying the fouled oxide.

In the older type of purifiers, using a number of boxes of relatively large area, with layers of oxide from 3 to 5 ft. in depth, it was usually assumed that 1 sq.ft. of area in a box would purify about 1500 cu.ft. of coal gas per 24 hours. At present, the tendency is to concentrate the oxide in two or three large circular boxes where the oxide is 10–15 ft. deep. Here the usual allowance is about 300 cu.ft. of gas per cu.ft. of oxide per 24 hours.

In testing the operation of the purifiers, we find that the first box removes the greater portion of the hydrogen sulphide, and that as the percentage of sulphur decreases it becomes increasingly difficult to remove it. The purifiers are usually arranged, therefore, so that at least one box is kept filled with fresh and active oxide to retain slight traces of sulphuretted hydrogen which might pass through the other boxes which remove the bulk of the impurity

With the repeated revivifications of the oxide, free sulphur accumulates to such a point (40 to 50 per cent) that it mechanically coats the iron, so that the efficiency of the oxide is greatly reduced.

The older and more inefficient forms of oxide require from ten to twenty revivifications before they are saturated while the later collodial oxides require from three to five.

When the cyanogen is not removed it combines with some of the iron, forming Prussian blue; this takes place at the surface, and further reduces the efficiency of the oxide. Some analyses of spent oxide are given showing the approximate content of Prussian blue, sulphur, etc., that may be expected.

ANALYSES OF SPENT PURIFYING MATERIAL

	Coal Gas.	Water Gas.
Times used	12	19
Weight per bus. dry	39.24 lbs.	61.61 lbs.
Original moisture	21.20%	7.31%
Analysis on dried sample		
Ferric oxide	26.71%	36.87%
Metallic iron	.06%	
Free sulphur	54.56%	36.84
Prussian blue	2.56%	
Tar	4.11%	13.54%
Shavings	12.00%	12.75%

When the gas was formerly purified with slaked lime, partially sulphided lime reacted with the organic sulphur compounds, and thus removed a considerable portion of them. With the present almost universal use of iron oxide, however, a much smaller proportion of the organic sulphur is taken out. The small percentage that is removed is undoubtedly due to its solvent action on the free sulphur present in the purifying materials. A number of processes have been proposed for the removal of organic sulphur, but in general they have not proven very successful.

One of the most successful processes for the removal of carbon bisulphide is that worked out by Carpenter and Evans in the South Metropolitan Gas Co., of Cleveland. In this process the gas is heated to temperature 750° F. and is then passed through externally heated tubes containing fireclay shapes saturated with a nickel salt. The carbon bisulphide combines with the hydrogen present in gas forming two molecules of hydrogen sulphide and settling free carbon.

On the Pacific coast the Hall and Papst process is used to some extent. This consists in heating the gas internally. Heater vessel filled with checker brick to a temperature of 1300° and 1600° F. This is claimed to cause a small loss in candle-power and results in reduction of about 70 per cent of carbon disulphide to H_2S.

Another process recently patented is based on the reaction of carbon bisulphide with water vapor at approximately 450° F. in the presence of colloidal ferric hydroxide. In this process the carbon bisulphide forms hydrogen sulphide and carbon dioxide. Experiments have indicated it

is possible to reduce the fixed sulphur compounds to a minimum of 8 or 9 grains per 100 cu.ft. This minimum seems to be independent of the original fixed sulphur compounds present and appears to indicate that in addition to the carbon bisulphide appreciable amounts of the other organic sulphur compounds are present such as mercaptans, thiophenes, etc. From 3 to 4 grains per 100 cu. ft. of a sulphur compound resembling the mercaptans have been isolated by experiments. The use of aniline in combination of metallic oxide that has been proposed for removing carbon bisulphide would probably give trouble, as it has been found that volatile compounds are formed by the gas in the presence of aniline and oxide that are deposited in burners, pilot tubes, etc.

Benzol Enrichment. In the ordinary process for the manufacture of coal gas the photogenic value of the gas is sometimes lower than that desired, and in the absence of a carburetted water gas plant, which is the most economical and efficient method of enriching and controlling the candle power of the gas, the most available method for enriching is the addition of benzol vapor.

Theoretically, coal gas should be able to carry over 3 per cent of benzol vapors at 32° F.; this would result in a gas of about 30 c. p. Practically, however, this result is not attained. This is due to the varying composition and resulting vapor tensions of the benzol vapor added and of the hydrocarbon vapors already present in the gas. The enriching power of benzol may vary from 13,000 to 38,000 candle feet per gallon; the usual commercial figures are from 20,000 to 24,000. In general, the efficiency of the enrichment decreases as the volume of vapor increases and with the higher initial candle powers.

The most successful results are now attained by scrubbing the gas with a heavy oil, thus removing all condensible constituents, and then re-enriching with a high grade of benzol.

Water Gas. The manufacture of water gas depends upon the decomposition of steam by the action of incandescent carbon. The gas made by this reaction is called "blue gas," and while it has a heating value of about 300 B.T.U. per cubic foot it is non-luminous. In order to render the flame luminous it is necessary to add some hydrocarbon that will liberate free carbon in the flame. Many early patents were taken out to do this, but the process did not become important until the Pennsylvania petroleums became commercially available.

The modern apparatus is the development of the Lowe apparatus that was patented in 1872–1875. In its present form it is a very efficient process, as every feature has been considered both from a theoretical and operative standpoint. The supply of air and steam is metered. The temperatures in the fixing chambers are controlled with electric pyrometers and the sensible heat in the off-going blast and illuminating gases is recovered in greater part in economizer boilers that return sufficient steam to operate the plant.

The apparatus shown in Fig. 220 has a capacity of 1,500,000 cu.ft. per day, but units having a capacity of 3,000,000 cu.ft. per day are in regular operation.

Operation. The operation of a modern plant, Fig. 220, is as follows: The generator is charged with the fuel through the coaling door *A*. After ignition, it is raised to a point of incandescence by a blast of air supplied under a pressure of from 16 to 20 ins. through the blast pipe *B*, passing through the interlocking valve *C*, which is so connected that it will be impossible for the blast and the gas to come together and thus cause explosions. The air passes down through the Venturi meter *D* and is controlled by the valve *E*, where it enters the generator beneath the

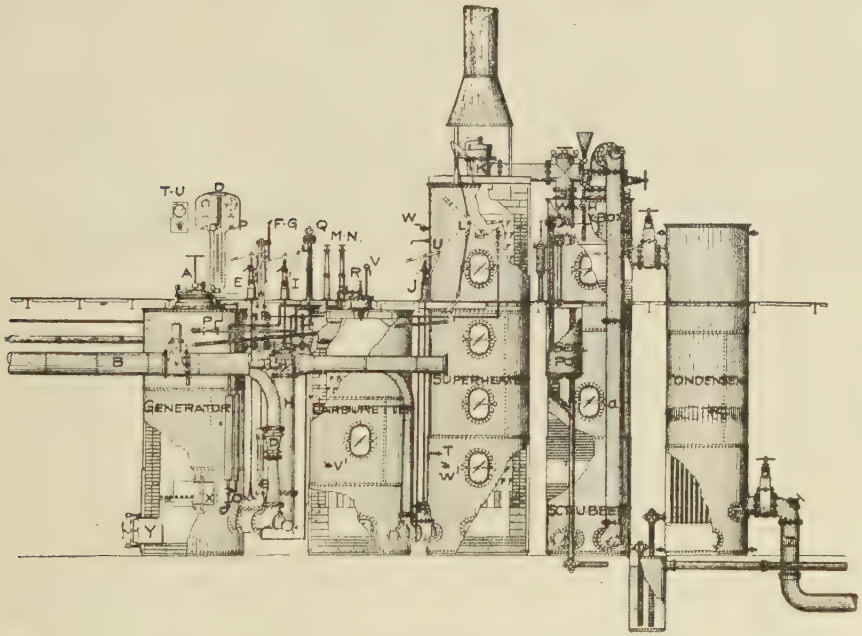


FIG. 220.—Modern Lowe Apparatus.

grate, passing through the fuel bed, where the reaction $C+O_2=CO_2$ and $CO_2+C=2CO$. The temperature of the fuel rises rapidly and a certain amount of producer gas is formed. This passes through the pair of valves *FG*, *F* being open during the blast, through the connection *H*, into the carburetter. The carburetter, which is a fire-brick lined vessel filled with checker-brick, is brought to the required temperature by the sensible heat in the blast products, and by the combustion of their CO by means of a secondary supply of air entering through the valve *I*. From the carburetter the products pass downward and up through the superheater, out through the valve *K* to the stack. When it is desired, the tertiary supply of air can be admitted through the valve *J* at the base of the superheater, causing further combustion, if desired, and local heating

in this part of the apparatus. Fig. 221 shows the economizer boilers for recovering waste heat from the gas and products.

When the carburetting and superheating vessels have been brought to the proper temperature, the fuel in the generator is very highly heated.

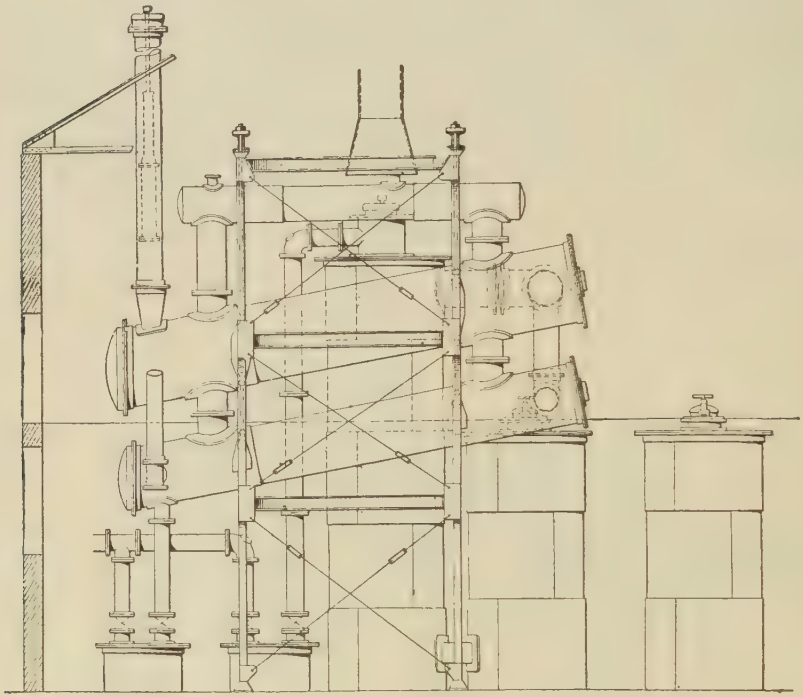


Fig. 216.—Waste Heat Boiler.

The air blasts are cut off in the order J, I, and E. The stack-valve K is closed by means of lever L, and steam is introduced by means of the valve M and the steam meter O beneath the grate. The steam passes up through the bed of incandescent fuel, where the reactions $C+H_2O=H_2+CO$, and the further general water gas reactions $CO+H_2O=CO_2+H_2$ take place. The water gas passes into the carburetter, where it meets the carburetting oil, which is measured by the meter Q and is sprayed into the carburetter through R. The sensible heat of the water gas and the high temperature in the surface of the checker-bricks vaporize the oil. The mixture of water gas and oil vapors then passes down through the carburetter, where the vaporization is completed, a considerable portion of the vapors decomposed and to some extent polymerized into fixed gases. Passing from the base of the carburetter up through the superheater, the temperature of the checker brick of which is very carefully regulated, the decomposition of the oil vapors is carried to the most advantageous point, and the resulting mixture is composed of

fixed gases, some condensible vapors and a small quantity of complex hydrocarbons, known as water-gas tar.

FORMATION OF CARBURETTED WATER GAS

	Top of Generator.	Base of Carburetter.	Middle of Superheater.	Top of Superheater.
Illuminants	.00	10.75	14.75	14.75
CO	39.75	33.05	30.70	30.65
H_2	50.00	43.05	34.60	31.35
CH_4	2.20	1.10	12.30	16.75
C_2H_6	.00	5.60	1.45	.30
CO_2	4.60	4.00	3.70	3.70
O_2	.35	.30	.30	.30
N_2	3.10	2.15	2.20	2.20

These pass out through the connection to the valve *K*, through the dip-pipe *S* into the wash-box, which acts as a hydraulic seal and prevents both the escape of the products of combustion during the blasting period and the return of the illuminating gases. In contact with the water in the wash-box, the temperature of the gas is reduced from 1200 or 1300° F. to about 190° by the vaporization of the water, and some of the tar is deposited. The gases pass out of the wash-box through the connection to the base of the scrubber, and rise through the staggered nest of wooden trays, where the entrained solid matter, considerable water, and some tar are deposited by impingement and the temperature is somewhat reduced. From the top of the scrubber it passes into the top of the condenser through the water-cooled tubes. By means of the cooling water the temperature is reduced to 150° F., and it passes out of the connection *Z* to the relief holder.

In the more modern plants the greater portion sensible heat of both the blast products and the illuminating gas is recovered and made available as steam by the employment of waste heat boilers. Fig. 216 shows such an installation. The apparatus consists of two fire-tube boilers and a steam drum. The lower boiler is used for the illuminating gas and the upper boiler is used for the blast gases. In operation the usual stack valve is closed and the gases enter the rear of the boilers and pass toward the front. In the case of the illuminating gases thence down through an auxiliary wash-box to the left of the regular wash-box and hence to the scrubbers and condensers.

The blast gases pass upward after passing through the upper boilers and then to an auxiliary stack and stack valve to the air.

By the use of these boilers the temperature of the exit gases is reduced to 400° F., thus affecting a considerable saving in condensing water and steam equivalent to 65–85 lbs. is generated.

In summer this is practically sufficient to operate the plant while the generating apparatus is in operation.

Fuel Used. The fuels used in the manufacture of water gas are anthracite and semi-anthracite coals and the various grades of coke. As they are used primarily as a source of carbon they should be high in fixed carbon, containing not over 7 per cent of volatile combustible, as some of this is liable to loss during the blasting period. The ash should be low and of high fusing point so that the formation of clinkers may be reduced to a minimum, although fuels containing as high as 25 per cent of very fusible ash can be utilized successfully. The fuel should be uniform in size to permit the free flow of the blast and steam and it should be low in moisture and sulphur. A table of typical analyses of the different classes of fuel used in the manufacture of water gas is given with the analyses and fusing points of the ash of some American coals

COMPOSITION OF ASH AND FUSING POINT

Ash in Coal.	7.67%	4.80%	5.49%	4.02%	8.93%	5.40%	5.18%
SiO_0	41.94	42.17	46.55	39.00	49.99	36.80	49.03
Al_2O_3	24.04	35.58	35.68	26.21	31.97	31.25	41.98
CaO	11.08	4.76	5.00	3.97	2.13	2.80	1.79
MgO	1.28	.....	1.00	.67	.81	tr.	tr.
Fe_2O_3	14.56	12.70	7.80	21.95	12.23	21.95	5.02
SO_3	4.61	3.21	3.76	4.44	.26	2.76	1.86
Alkalies and undet.	.49	1.68	.21	3.76	2.61	4.44	.32
Color of ash	Terra cotta	Terra cotta	Lt. gray	.....	.....	Lt. gray	Lt. gray
Fusing point, ° F.	2147°	2280°	2350°	2390°	2570°	2640°	3020°

COMMERCIAL GENERATOR FUELS

	Moisture.	Volatile Comb.	Fixed Carbon.	Ash.	Sulphur.	Fusing Point of Ash. ° F.
Anthracites:						
Buck mountain	3.87	4.08	77.52	14.53	.40	2750
Lackawanna	3.92	3.48	82.11	10.49	.63	2714
Lehigh	3.44	3.11	84.11	9.34	.50	2610
Pittston	3.91	5.16	73.07	17.86	.90	2962
Susquehanna	2.30	5.00	84.14	8.56	.66	3115
Cokes:						
West Virginia	.69	.83	91.11	7.31	.49	2282
West Virginia	.80	.88	85.53	12.79	.66	2610
Virginia	.70	.86	90.81	7.63	.46	2606
Alabama	.60	.69	87.01	11.70	.77	2715
Kentucky	.02	.56	94.58	4.84	1.04	2250

Enriching Oils. The oils available for enriching purposes vary in their composition in the different fields. The oils from Pennsylvania, Ohio, Indiana, and Illinois are composed principally of the paraffine

and olefine series; the oils from Kansas and Indian Territory differ somewhat according to their gravity, the lighter oils containing considerable paraffine while the heavier oils contain some paraffines but principally naphthenes. The Texas oils contain almost no paraffine, but contain a considerable proportion of complex hydrogenated ring compounds; they are made up of members of the C_nH_{2n-2} and C_nH_{2n-4} series. The California oils are made up almost entirely of complex ring compounds. The Louisiana oils vary with their gravity, some resembling Texas and others the California oils.

The crude Mexican oils generally contain too large a proportion of asphalt to permit their use as enriching agents. Some of the distillates apparently contain a very high percentage of paraffine hydrocarbons while others contain a very low percentage and contain such a high percentage of aromatic and olefine hydrocarbons that they are of rather low value for enriching purposes.

With the introduction of "cracking" processes for increasing the yield of gasoline in the refining of petroleum the character of the gas oils available for enrichment has changed considerably. The paraffin content is considerably reduced and the proportion of aromatic and olefine content is greatly increased so that the enriching value is greatly decreased.

The following table gives some of the physical characteristics of a number of enriching oils that are at present in use in the United States.

CHARACTERISTICS OF GAS OILS

Field.	Pa. and W.Va.	Kansas.	Oklahoma.	Mexican.	Indian Ter.
Specific gravity.....	.8470	.8540	.8667	.8550	.8811
Refractive index.....	1.4673	1.4782	1.4830	1.4792	1.4892
Coke, % by wt.....	.31	.27	.35	.19	.66
Maximum fraction .	600-650° F.	600–650° F.	550–600° F.	550–600° F.	550–600° F.
Percentage by vol...	58.6	25.1	38.2	14.8	30.0
Specific refraction...	.5454	.5553	.5577	.5533	.5559
Hydrogen.....	14.10%	13.39%	12.86%	12.58%	11.81%
Bromine number....	5.3	10.1	13.0	15.5	25.3

As enriching agents it seems that the paraffines are the most valuable, the presence of double carbon linkages and rings reducing the efficiency. Where ring compounds are present, however, the more fully hydrogenated are the more valuable.

The yield of tar on gasification is an indication of the presence or absence of complex hydrocarbons in the oil. In the oils from Pennsylvania it will run from 8 to 10 per cent of the oil, while the Texas and California oils will yield from 15 to 18 per cent, denoting the presence of complex ring and asphaltic compounds.

COMPARATIVE YIELD OF WATER GAS TAR FROM DIFFERENT OILS

Naphthas,	paraffine base,	2–4	per cent by	volume of oil.
Gas oils,	paraffine base,	6–10	"	" "
Crude oils,	paraffine base,	8–12	"	" "
Gas oils,	asphaltic base,	10–15	"	" "
Crude oils,	asphaltic base,	12–18	"	" "

The change in the character of the gas oil has been reflected in the character of the tars produced.

The accompanying table gives a comparison of the tar made from several typical present day gas oils.

TABLE OF WATER-GAS TAR DISTILLATION

Oil.	Oklahoma Ind. Territory.			Texas.		
Specific gravity	1.0604			1.0922		
Water	3.0%			.6%		
Naphthalene	Trace			Trace		
Coke	25.41%			26.02%		
Fraction. ° F.	Per Cent By Weight.	Specific Gravity.	Ref. Index.	Per Cent By Weight.	Specific Gravity.	Ref. Index.
Up to 300	3.06	.8973	1.5330	1.20		
300–350	3.90	.9140	1.5472	1.63	.9172	1.5318
350–400	4.92	.9473	1.5582	3.91	.9488	1.5577
400–450	9.15	.9705	1.5758	11.12	.9720	1.5696
450–500	14.45	.9882	1.5870	12.65	1.0047	1.5946
500–550	11.55	1.0202	1.6065	7.50	1.0249	1.6093
550–600	3.15	1.0403	1.6162	12.23	1.0439	1.6214
600–650	5.68	1.0568	1.6381	11.93	1.0877	1.6624
650–700	8.22	1.0823	1.6558	5.67	1.1278	1.6959
700–+	9.32	1.1212		6.03	1.1755	
Coke	25.41	.....	.....	26.02		
Total	98.81	.....	.....	99.89		

The reactions involved in the formation of oil gas have received very extensive study during the past few years with particular reference to the possibility of increasing the production of low-boiling hydrocarbons, such as benzene, toluene and gasolene. There has been a tendency to emphasize the formation of naphthenes as secondary products. As a result of this study we have acquired a considerable amount of data regarding the general course of the reactions and the most favorable temperatures for emphasizing the production of certain constituents.

In general, however, the reaction involved following much the same lines as those occurring during the latter stage of the carbonization of coal. The principal difference being that in the manufacturing of carburetted

water gas the temperatures involved and the time of contact is under much more exact control, in this connection, it may be noted there is a considerable larger proportion of toluene to benzene and a smaller proportion of naphthalene formed than in the manufacture of coal gas.

The use of a small laboratory apparatus for the study of the behavior of gas oil has been of great service in predicting the probable usefulness of the oil for carburetting purposes, while considerable advance has been made in chemical methods looking to the determination of analytical constants that will permit predicting useful qualities.

The products formed with increasing temperatures seem to follow in general the reactions that were discussed under the distillation of coal; the illuminants decrease and the hydrogen increases while the paraffines remain about stationary.

EFFECT OF TEMPERATURE ON DECOMPOSITION OF OIL

Temperature. C.	Gas per Gal. Cu.Ft.	Tar. Per cent.	Coke. Per cent.	Olefines. Per cent.	Paraffines. Per cent.	Hydrogen Per cent.
711	56.4	28.0	1.83	38.0	48.0	11.1
741	61.5	29.4	2.43	33.8	48.3	14.1
751	63.7	26.2	3.63	31.3	50.3	13.5
789	68.0	24.2	3.45	25.0	49.2	19.1
832	80.3	11.9	12.43	13.1	47.0	33.6

The influence of the high partial pressure of the hydrogen is especially marked in the formation of carburetted water gas, as the blue gas contains nearly 50 per cent of hydrogen. The hydrogen inhibits the decomposition of the primary products and the splitting off of more hydrogen, which unites with the complex residues resulting in a higher percentage of olifines, somewhat less gas and more tar. The following table shows the composition of oil gas at a given temperature, and the calculated and observed mixtures of oil and blue gas:

CALCULATED AND OBSERVED COMPOSITION OF CARBURETTED WATER GAS

	Blue Gas.	Oil Gas.	Calc. Carb. W. G.	Obs. Carb. W. G.
Illuminants	.0	36.6	9.5	14.8
CO	39.8	1.1	29.7	30.6
H_2	50.0	13.3	40.5	31.4
CH_4	2.2	40.4	12.1	16.8
C_2H_6	.0	6.9	1.8	.3
CO_2	4.6	.5	3.5	3.7
O_2	.4	.....	.3	.3
N_2	3.1	1.3	2.6	2.2

This shows the increased illuminants and decreased hydrogen and increased tar. It should be noted also that in practical operation we obtain about 6000 candle feet per gallon of oil in carburetting water gas while we should only obtain about 3000 candle feet if the oil gas were used alone.

In determining the practical enriching value of an oil it is run in a machine for some time with different temperatures in the fixing chambers and the candle feet per gallon calculated and plotted against the temperature. The maximum value and its corresponding temperature is then easily determined. A typical curve of this kind is reproduced below, Fig. 222.

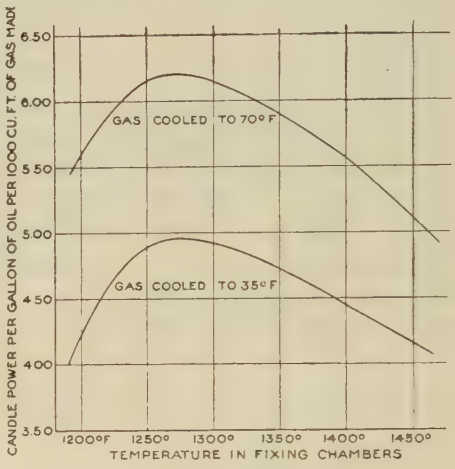


FIG. 222.

In considering the theory of the formation of the blue gas or water gas proper we have the two general steps—storing heat in the fuel bed by the combustion of a portion of the fuel with a blast of air, and utilizing this heat in decomposing steam with the formation of the water gas which is an endothermic reaction.

During the blasting period the primary reaction is probably:

$$C+O_2=CO_2 \quad \text{or} \quad 2C+O_2=2CO.$$

These equations are connected by relation $CO_2+C=2CO$, which is the equation for the equilibrium. Clement and Haskins have given the following expression for the value of K at any temperature, viz.:

$$K=\frac{C_{(CO)}}{C_{(CO)}}.$$

$$\ln K=-\frac{20235}{T}+1.035\ \ln T-.001564T+8.604,$$

and they found that with coke the following percentages were in equilibrium at different temperatures:

Temperature.	Carbon Monoxide.	Carbon Dioxide.
°C	%	%
900	83.2	16.8
1000	94.5	5.5
1100	98.1	1.9
1200	99.4	.6
1300	99.7	.3

It must be remembered, however, that in commercial producer gas the presence of the nitrogen lowers the partial pressure of the carbon monoxide, and thus slightly increases the ratio $CO \div CO_2$ over that given in the table. It is found that the time of contact is very important, and that with the increasing temperatures the increase in the coefficient of the reaction velocity is about ten times the increase in the diffusion constants, so that velocity of the chemical combination is the determining factor in this reaction.

It is found that the different forms of carbon do not react alike, charcoal reacting most rapidly, coke next, and anthracite most slowly. In the second stage of the process, that of the decomposition of steam,

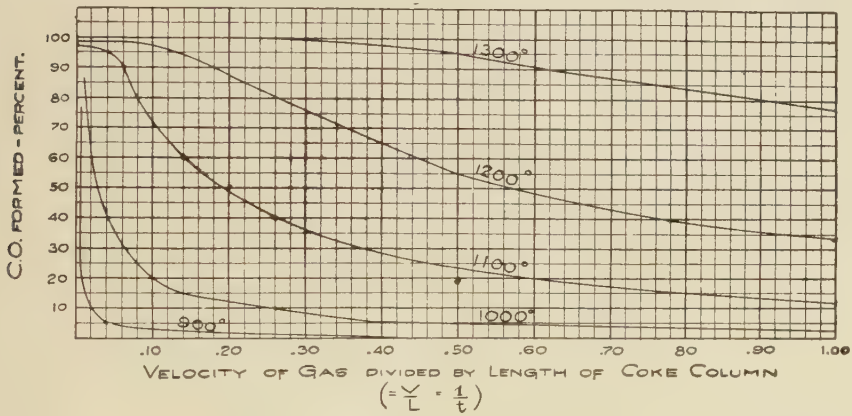


FIG. 223.

we have two reactions: $C+H_2O=CO+H_2$, and $C+2H_2O=CO_2+2H_2$. These products are then related according to the two reactions $CO_2+H_2=CO+H_2O$, and by the reaction previously discussed, $CO_2+C=2CO$. The calculation of the constants of the water gas reaction is complicated by the uncertainty regarding the specific heat of the reacting bodies at high temperatures. Haber gives the following equation for the value of K at equilibrium at temperatures of from 1250° to 2700°F.

$$\log K = -\frac{2232}{T} - .08463 \log T - .0002203T + 2.5084.$$

From experimental work that has been done on this problem, it is apparent that while the water gas reaction ceases to readjust itself to changes of temperature at about 2550° F. in the Bunsen burner, yet in the water gas generator it seems to adjust itself down to very moderate temperatures. This is probably due to the influence of the ash on the surface of the coal. It is also assumed that in the generator while the gases may be in equilibrium with themselves, they are not in equilibrium

with the carbon in the fuel bed. In Fig. 223 are given some experimental results obtained by Clement and Haskins, using coke as fuel, with the time of contact of the steam equal to two seconds.

In the practical operation of water gas apparatus the efficiency of the production of blue gas will be dependent upon the temperature of the blast gas and water gas issuing from the fire; the percentage of CO or excess air in this blast gas, and the percentage of undecomposed steam in the blue gas, assuming, of course, that we are operating the generator so as to produce a reasonably low percentage of CO_2. These conditions will probably be influenced by the rate and time of passage of blast through the fire. There are two divergent views on this subject. According to one writer, when the rate of passage of blast is sufficiently great in proportion to the depth of fuel, CO will not be formed, but only CO_2. Another writer, on the other hand, finds very little change due to the rate of passage of the gas, and believes that the efficiency of the blow is dependent on the temperature of the fire, and is principally a function of the length of time.

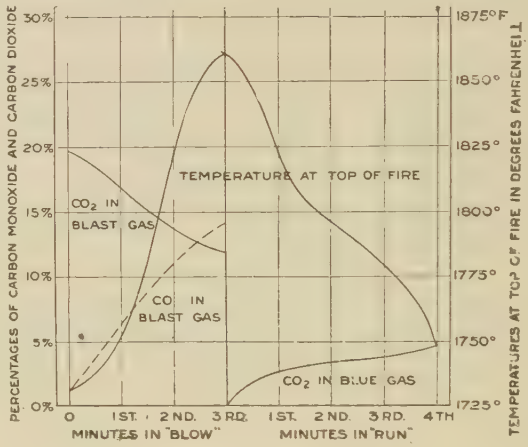


FIG. 224.

Apparently, an increase in the rate of blast, Fig. 223, will give a higher average temperature of the fire, which results in somewhat increased temperature of the issuing blast gases, with slight decrease in the percentage of CO. It is quite conceivable, in view of the theory that the speed of the reaction $CO_2+C=2CO$, will increase so rapidly with increase in temperature that we cannot sufficiently decrease the time of contact to prevent the formation of considerable quantities of CO.

Increasing the rate of passage of steam will apparently reduce the temperature of the outgoing water gas, which is favorable to economy, but this is more than offset by the smaller percentages of steam decomposed, and the consequent waste of both excess steam and its sensible heat, and furthermore, by the greater percentage of CO_2 in the blue gas. In general, all of the writers assume the importance of the slow rate of passage of the steam.

The temperature and condition of the generator fire, Figs. 224 and 225, appear to be the most important conditions. The capacity of the fuel bed increases with an increase in the temperature, resulting in a larger yield and

a more perfect decomposition of the steam, and a more favorable composition of the blue gas. On the other hand it increases the sensible heat of the off-going blast products and the blue gas, and results in an increased percentage of CO in the blast products, both of which are unfavorable to fuel economy.

The necessity of producing a certain amount of available combustible in the blast gases to maintain the fixing chambers at the proper temperature somewhat complicates the operation when carburetted water

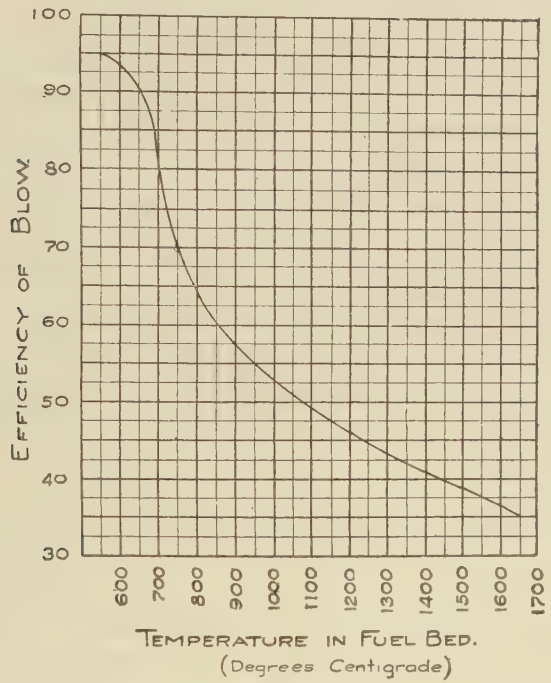


FIG. 225.

gas is manufactured. With indifferent control of the operating conditions a large excess of CO is always produced with some fuels.

Modern practice attempts to bring the whole fuel bed to a uniform temperature and to reduce the variation or range of temperatures as far as possible, thus enabling the temperature in the active zone in the fuel bed to be maintained at a point where the clinker can be controlled. This results in a minimum loss of sensible heat incurred by the offgoing gases and yet a satisfactory decomposition of the steam is secured at an increased rate.

The use of two generators that are blasted in parallel but are connected in series, during the gas-making period, is an endeavor to secure more uniform fire conditions.

From the theory of the reactions underlying the combustion of the

coal and the formation of water gas, it will be seen that many of the requirements are contradictory. It is therefore necessary to arrange our operating conditions so as to secure the most efficient compromise, remembering that many of the theoretical processes will yield very efficient results under test conditions, but may utterly fail to satisfy the commercial requirements as to overhead charges for capital invested and the labor cost of operating.

The following table gives a set of operating conditions that were in one case found to yield satisfactory results.

OPERATING CONDITIONS

Size of set	8 ft. 6 in.
Area of grate	33.2 sq.ft.
Fuel used, oven coke	
Oil used, Lima gas oil	
Candle-power of gas made	25.2 at 70° F.
Candle-power per gallon of oil	6 at 70° F.
Carbon in generator per M	25 lbs.
Temperature base of superheater	1461° F.
Temperature top of superheater	1300° F.
Length of blow	3 min.
Pressure of blast	20 ins. water
Rate of blast cu.ft. per sq.ft. grate per minute	129 cu.ft.
Generator air used per M. cu.ft. of gas made	1520 cu.ft.
Carburetter air	800 cu.ft.
Length of run	4 min.
Per cent up runs	64.8
Per cent down runs	35
Rate of steam pounds per sq.ft. grate per min.	2.1 lbs.
Steam used per M. cu.ft. of gas made	33 lbs.
Gas made per sq.ft. grate per hour	1.910 cu.ft.

The condensation and purification of carburetted water gas differs somewhat from that of coal gas, in that the water gas is more fully saturated with hydrocarbons which must be preserved and retained in the gas to secure its proper illuminating value.

In this connection it is interesting to note that typical coal gas might be expected to contain 1.7 gallons per 1000 of benzol; .045 gallon of toluol, and .055 gallon of solvent naphtha; water gas will contain about the same, or little less solvent naphtha, will contain about twice as much toluol and probably slightly more benzol.

The greatest care must be taken in regard to the temperatures employed throughout the condensing and purifying system to avoid suddenly shocking the gas, and we endeavor as far as possible to keep the gas closely in equilibrium with the surrounding condensate.

In this connection reference should be made to the determination of the candle-power at a constant temperature, and the use of a hygrometer in the determination of the dew-point of the hydrocarbon vapors in the gas, as aiding in the delivery of gas of a uniform candle-power at

distant points and as an adjunct in arriving at correct condensation conditions. The gas leaving the wash-box at a temperature of about 190° F. passes through the scrubbers and primary condensers into the relief holder. The bulk of the tar will now have been deposited. From the relief holder it is drawn by means of the exhausters, and pumped through the secondary condensers and tar extractors, which are usually of the P. & A. type described under coal gas, into the purifying house. In case the P. & A. type of extractor is not used, vessels filled with shavings are used to mechanically filter out the entrained liquids.

The purification of water gas is carried on under the same general conditions as those surrounding the purification of coal gas, except thatit is desirable to keep the temperature at purifiers above 100°C, and this temperature should be held as uniformly as possible. This is to prevent the gas changing suddenly in temperature, and thus getting out of equilibrium with the purifier material, which is saturated with condensate.

The following range of temperatures is an example of an average of working conditions under which the manufacturing results were excellent, and which would justify the conclusion that the gas was being properly handled. It should be remembered in this connection that it is quite probable that with different raw materials and a different design of plant these temperatures would require modification:

Temperature of the atmosphere	66° F.
Top of superheater	1200
Outlet of wash-box	190
Inlet of scrubber	180
Inlet of relief holder	154
Inlet of exhauster	115
Inlet of tar extractor	113
Inlet of purifier	103
Outlet of purifier	85
Outlet of station meter	85

Fig. 226 gives the plan of a moderate size water gas plant. It will be noted that the gas passes from the machine through the preliminary scrubbers and condensers to the relief holder, hence through the final condensers, exhauster, through the purifiers, meter and storage holder, then through the governor to the distribution system.

General Processes. We have heretofore considered only the manufacture and purification of the several commercial gases, as these processes have differed considerably for each class. We will now take up several steps that while they more properly belong to the distribution of the gas, yet they are undertaken at the plant and may now be briefly considered here as being common to all the various classes.

After the gas passes the purifier it is metered in order that a proper

check may be kept upon manufacturing operations. The volume of gas made is usually corrected to 60° F. and 30″ Barometer.

The usual form of meter in use, Fig. 227, is the wet drum meter, which operates by the displacement of a water-sealed drum, and this is the only form of meter that actually isolates a definite volume of the gas and records

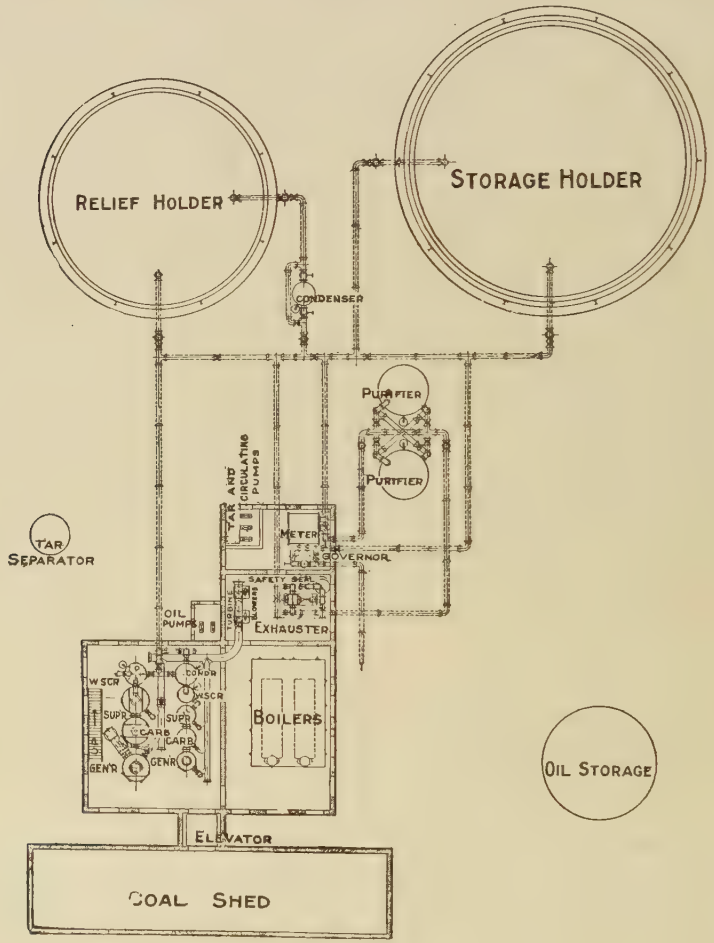


FIG. 226.—Plan—Water Gas Plant.

it. Recently the so-called dry rotary meter has been introduced. In this form the velocity of the gas passing through definite orifices is measured and recorded by a form of anemometer. Another form of meter which has just been introduced is the electric meter, which automatically records the mass, and therefore volume, at a definite temperature of the gas by the rise in temperature of the stream of the gas that has had a definite quantity of heat added electrically. In large installations, particularly

in the coke oven industry, where large volumes of gas have to be measured and absolute accuracy is not required, Venturi meters have been used with automatic integrating mechanism. These have been successfully used where the flow is fairly uniform and their use was desirable owing to low installation cost.

From the meters the purified gas passes to the storage holders, Fig. 228, showing three types of construction. The holder proper, or bell, is built of thin sheet iron or mild steel supported in a structural steel guide-frame. The holder if large is composed of several sections to reduce the depth of the tank in which it is sealed. The various sections are

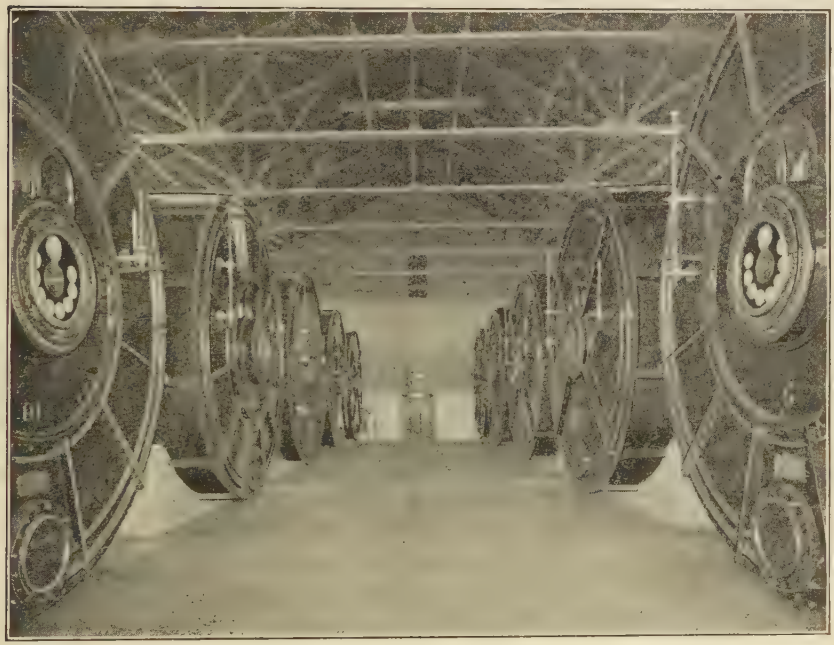


Fig. 227.—Station Meters.

joined with water seals which in climates where freezing weather is prevalent must be heated to prevent the water from freezing and damage to the holder. The tanks are either of brick or concrete built in the ground or of steel above the ground. Owing to the great weight of the water and steel composing the holder the foundation must be carefully prepared, especially where the tank is of brick or concrete.

In order to secure proper and adequate pressure conditions, the gas as it passes out of the holders is passed through governors which automatically maintain a constant pressure or in some cases increase and decrease the pressure in accordance with the varying rate of flow.

Laboratory Control. The laboratory control of the gas is usually confined to the determination of the illuminating and heating values, and the determination of the impurities, as ammonia, hydrogen sulphide and organic sulphur compounds, and the volumetric determination of the constituent gases.

The illuminating value is usually determined with a Bunsen photometer, Fig. 229, using the Leeson Star disks in the comparison head. The pentane lamp is now considered the standard of light of the American

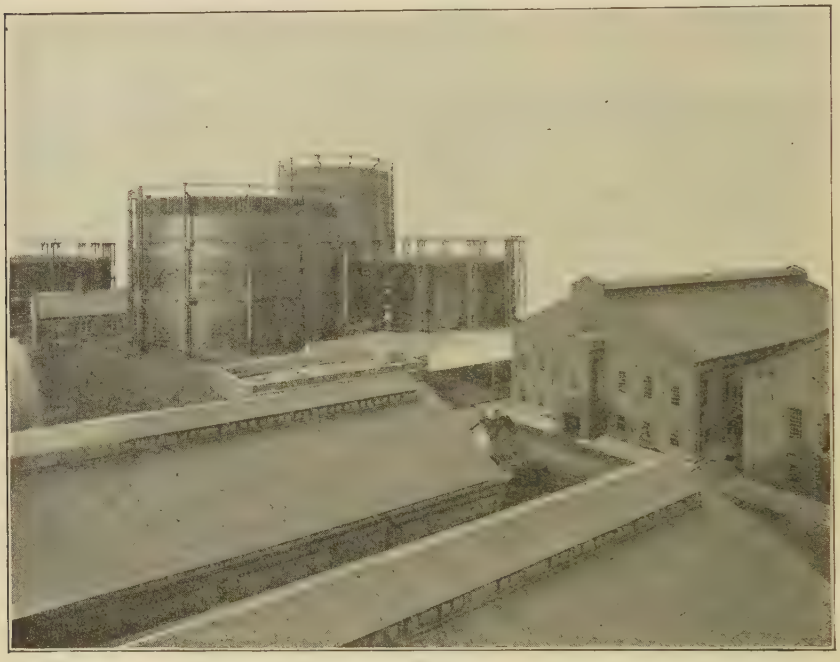


Fig. 228.—Showing the Gasometers filled and ready for the consumer.

Gas Industry. Its value as compared with other sources is given in the table below:

Value of International Candles

(See *Electrical World*, May 27, 1909, p. 1259)

1 pentane candle = 1 Bougie decimale;
= 1 American candle;
= 1.11 Hefner unit;
= .104 Carcel unit.

In connection with the determination of the illuminating value, attention is called to the report of the Committee on Photometry, presented to the American Gas Inst., 1907. The calorific value of

the gas is usually determined in a Junker, or modified Junker, calorimeter. For details regarding the standard methods of conducting this test, recourse should be had to the report of the Committee on Calorimetry of the American Gas Inst. for the years 1908 et seq. See also Chapter III.

The ammonia is determined by absorption in standard sulphuric acid; Hydrogen sulphide by titrating the gas directly with a standard solution of iodine, or by absorption first in cadmium chloride. The organic sulphur compounds are determined by burning a definite quantity of the gas in an atmosphere of ammonia. The products are condensed and the sulphur determined as sulphate by precipitating with barium chloride.

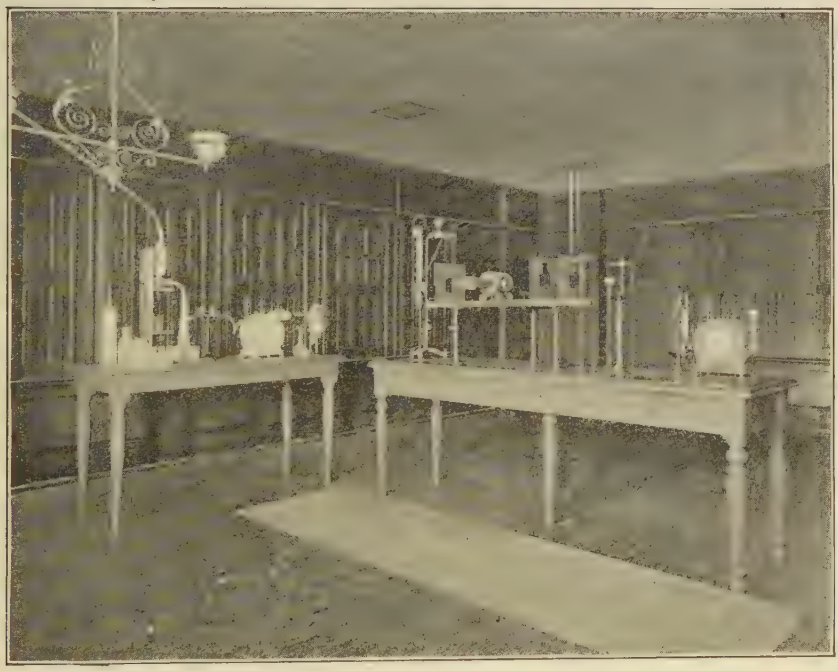


Fig. 229.—Photometer Room. Also showing apparatus for testing sulphur content.

In the analysis of the gas itself for its constituents, a modified form of Hempel apparatus is usually employed. The burette is provided with a manometer tube and water jacket, which enables the volume to be corrected automatically to a definite temperature and pressure. The constituents usually determined are illuminants by absorption in bromine water, carbon monoxide by absorption in an acid solution of cuprous chloride, CO_2 by absorption in potassium hydroxide and oxygen by treatment with yellow phosphorus. After the absorptions are completed a portion of the residue is mixed with air and exploded, and the contraction and CO_2 formed determined.

Another portion of the residue is mixed with air and subjected to partial combustion over palladium black, the contraction and CO_2 formed being again determined. From this data it is possible to calculate the percentages of hydrogen, methane, ethane and any residual CO which may have escaped the absorption.

The nitrogen is determined by difference, and is checked by determining the amount left in the residue from the explosion.

While a number of methods have been proposed for the determination of the benzol vapors in the gas, none of them has given very satisfactory results.

At the present time especially in connection with the operation of benzol recovery plants more accurate methods for the formation of benzol homologs in the gas are required. The most satisfactory determinations are made by scrubbing from 500 to 1000 cu.ft. in a small tower scrubber with a high-boiling paraffine oil or cotton-seed oil, using sufficient oil so that the light oils absorbed will not exceed 2 to $2\frac{1}{2}$ per cent. The light oils are then recovered by distillation with live steam and the total quantity noted after washing with sulphuric acid and soda to remove the unsaturated hydrocarbons.

The relation, however, of benzol, toluol and xylol are determined by fractional distillation with a dephlegmator.

Attention is called to a paper by Mr. E. A. Earnshaw, Franklin Institute, for details in the analysis of gases.

All Oil Water Gas. Directly related to the manufacture of carburetted water gas is the so-called all oil water gas which is used so extensively on the Pacific Coast where there is an abundant supply of cheap fuel oil.

The general theory of this process is that of the pyrodecomposition and polymerization of the oil hydrocarbons as in the Pintsch process, and to some extent carburetted water gas.

In the present form of apparatus which is illustrated in Fig. 230, there are two fire-brick lined shells in the form of a U, with one leg longer than the other, the shorter leg serving as the primary generator while the longer leg serves as a superheater. Both shells are filled with checker-brick. The gas take-off for the blast gases is at the top of the longer leg while the illuminating gas take-off is in the middle.

In the operation of the set, oil and steam are blown into the top of the primary generator while the blast is admitted in the center. The blast is turned on for about three minutes before the oil at a pressure of about nine inches, at the end of this time the oil is turned on at a pressure of about 8 lbs., the atomizing steam at 35 lbs. The heating period is about twelve minutes; at the end of this time the blast is cut off, the valve opened connecting with the wash-box, and the gas-making oil is injected as before, with steam, through another set of nozzles. The gas-making nozzles are located both in the primary generator and also in the top of the secondary generator, so that the flow of oil through

the machine can be regulated according to the heat carried in the checker work in all parts of the set. The oil is admitted to the top of

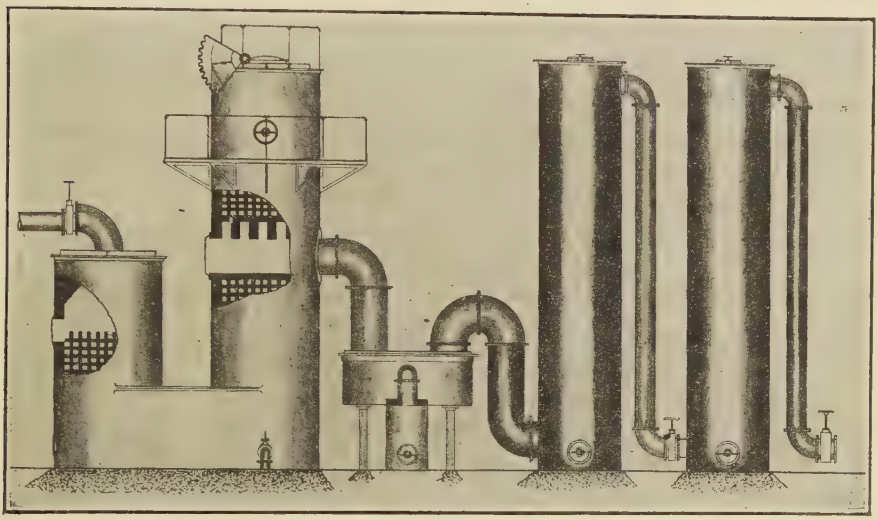


Fig. 230.—Jones' All Oil Water Gas Apparatus.

the primary generator at first quite rapidly, it is then gradually reduced during the run until at the eighth minute it is flowing at about one-third the initial rate per minute. The oil is admitted to the secondary generator at a slightly slower rate and is gradually reduced in the same proportion. The last two minutes of the run the oil is cut off and the steam pressure is raised to 100 lbs., and allowed to remain at this pressure for two minutes in order to purge the machine.

The heats in the machine are controlled by the appearance of the overflow from the wash-box, the presence of tar showing that the heat is too low while lampblack from the overflow in the first scrubber shows that the heat was too high. The make of gas per minute during the run is a very good indication of the heats carried and is an index to the proper length of the run.

In the larger machines about 16 per cent of the total oil used is burned during the heating run so that where the total oil per thousand runs about $8\frac{6}{10}$ gallons, about $1\frac{4}{10}$ gallons per thousand are used during the heating run and $7\frac{2}{10}$ gallons during the gas making run.

An average analysis of the oil gas made with a heavy California crude is as follows:

Ills	7.01%
CO	9.21
H_2	39.78
CH_4	34.64

CO_2	2.62
O	.16
N	6.58
C. P.	19.69
B.T.U.	680
Sp.gr.	.482

In general this gas resembles coal gas in many of its constituents much more closely than it does water gas. But there is every reason why this should be so as both of these gases are formed by the pyro-condensation of hydrocarbons.

The formation of the all oil water gas being almost identical with the second and third stages of the coal gas distillation except that in the case of the oil gas the temperature conditions and time of contact are under much more exact control. In general all that has been said previously in reference to the decomposition of the hydrocarbons applies with equal force in manufacture of the oil gas in this apparatus.

In the early days of this process the working conditions were not well understood and the operation of the machines resulted in enormous accumulation of lampblack from excessive and irregular temperatures carried in the apparatus. Now, however, with the control that is exercised over the operation of the set and in addition the better design, the apparatus has resulted in an almost total elimination of the trouble and nuisance due to lampblack. The bulk of the lampblack is now removed in a self-cleaning wash-box in which the lampblack is washed from the gas by a large quantity of water, which prevents the formation of large lumps.

From the wash-box the gas passes through scrubbers filled with wooden trays similar to those used in the carburetted water gas apparatus; as there are no by-products to be saved a rather excessive amount of water is supplied to the scrubbers. In some of the plants three scrubbers are used applying from 10 to 15 gallons per thousand per scrubber, or a total of say 40 gallons per thousand. The water from the wash-box and scrubbers is run into the lampblack separator where the lampblack is removed. The lampblack as taken from the separator contains about 60 per cent of water. This is piled in heaps and allowed to drain until it contains about 20 per cent, it is then used for fuel either under the boilers or in water gas apparatus. In the larger sets about 20 lbs. of lampblack are made per thousand feet of gas.

A great advantage of this type of apparatus is that it can be built and handled in large units, so that the operative labor is reduced to a minimum and from the fact that no time is lost in clinkering. The machines can be depended upon to produce their gas continually so that only a very low holder capacity is required.

Of the available oils in California, it has been found that those highest

in gravity give the best results, or in other words, that the hydrocarbons present in the oil are all about equally valuable, so that the oil yielding the greatest weight per gallon will naturally give the greatest number of cubic feet of gas. This result rather bears out the idea that has been gaining ground in the East where the heavier grades of enriching oil have been tried out and experimented with more thoroughly. The

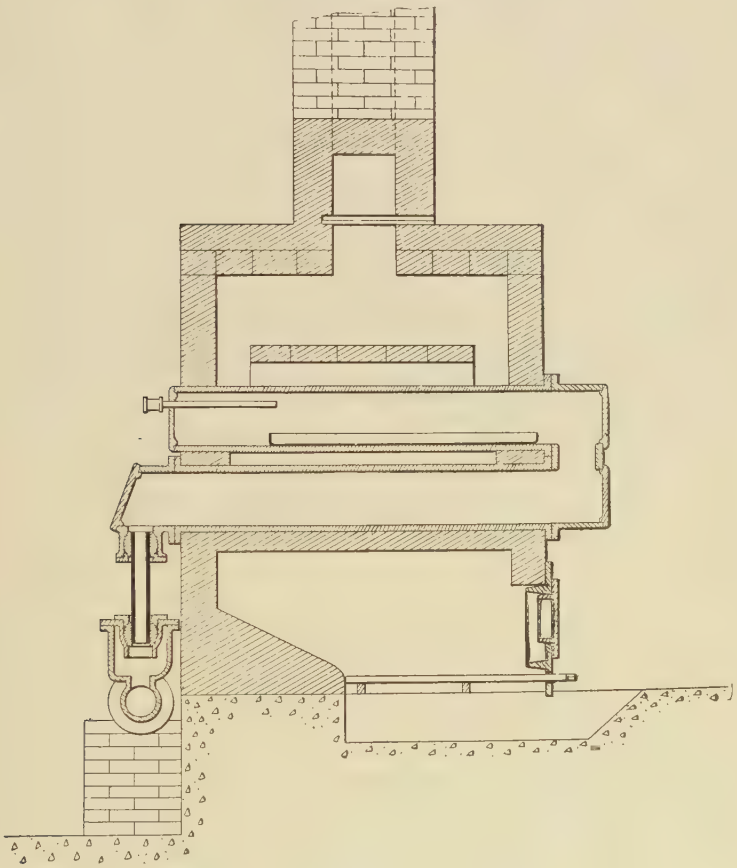


Fig. 231.—Pintsch Retort Bench.

sulphur content of the California oils varies quite widely, ranging from a fraction of a per cent to above 4 per cent. It has been found that where the sulphur does not exceed one per cent the gas is easily purified with iron oxide in simple purifiers.

Pintsch Gas. Another commercial adaptation of oil gas is that known as Pintsch gas. Pintsch gas is simply an oil gas compressed to about ten atmospheres and was developed originally for the lighting of railway passenger cars. The Pintsch patents were taken out about 1870.

In this system the oil is first decomposed in a double iron retort, set in a regular coal gas bench, an outline sketch of which is shown in Figs. 231 and 232. The oil is introduced at the front of the upper retort and falls upon a movable tray, which collects most of the

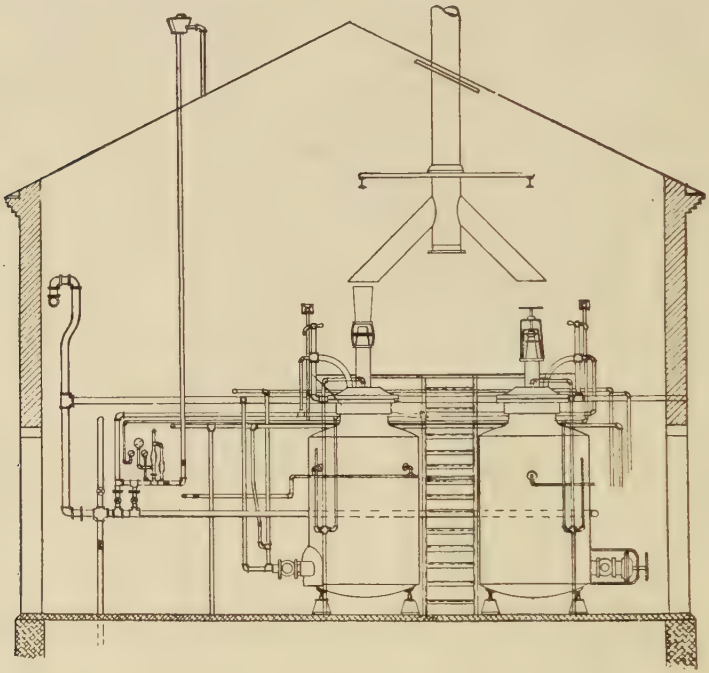


Fig. 232.—Pintsch High Pressure Plant.

carbon formed. The gas and vapors thus produced pass to the back of the upper retort down and out through the lower retort to a hydraulic main located in front of the bench. The crude gas is passed through a dry scrubber, condenser and purifier and after metering is collected in a low pressure holder, very similar in all respects to the processes employed in condensing and purifying coal gas. The gas is then compressed, generally in a two-stage compressor, into the storage cylinders. Every precaution is taken to remove the condensation thrown down by the compression, so that the gas in the cylinders will be thoroughly dry. The pressures employed vary from 10 to 14 atmospheres, the latter figure being common in the United States. In some plants, fireclay retorts are employed; in these the oil is passed through the back of the retort and is taken off at the front, so that a single retort suffices. The ordinary form of carburetted water gas apparatus has been used also in the manufacture of Pintsch gas. After the regular blow, instead of turning on the usual supply of steam, only a very small supply is used, just sufficient to clear the machine of the oil gas made. The success

of this work has resulted in the adaptation of a special form of apparatus for generating the Pintsch gas, very similar to the apparatus employed in California for the manufacture of oil gas. In this case, however, the fuel used in the heating run is a tar obtained as a by-product. This is injected into the top of the generator with steam and air until the proper temperature is acquired, then gas oil under pressure is injected, the vapors formed pass down through the heated checker-brick, and are subjected to the same transformations that occur in the water gas set. The heating period is about five minutes, the gas-making period from 6 to 8 minutes. About 1500 cu.ft. of gas are made per run. It has been found that the candle power is increased by about 10 per cent over that obtained in the retort form of apparatus. A late development of the system is a generation of the gas at high pressure, in a generator built of heavy steel plates, so that the whole operation takes place at high pressure. A small amount of steam in this type of apparatus is injected with the oil. The steam acts as a carrier but does not react with the oil or carbon formed, as the temperature, about 670°, is too low for the reaction to take place. A mixture of gas, tar and water is charged into the store holder at a pressure of about 14 atmospheres. It is purified under pressure and then stored directly into the cylinders. The average composition of the compressed gas is as follows:

Methane	50 to 60 per cent
Illuminants	30 to 40 "
Carbon monoxide	.5 "
Hydrogen	3 to 5 "
Sp. gr. from	78 to .85

The candle power of the gas when tested in open flat flame burners, does not do the gas justice, as it only averages about 40.

The design of the Pintsch regulator and its perfect operation under severe conditions has contributed very greatly to the successful application of the Pintsch system.

At present in addition to its use in railroad lighting, it is extensively employed in buoy lighting. The gas under a pressure of 100 atmospheres is compressed in cylinders which form the body of the buoy. On one gas charge these buoys were run to 528 days. These buoys can be provided with automatic mechanism so that the light can be operated either as a continuous light or in any desired sequence or flashes.

Blau Gas. Another modification of the Pintsch gas is known as Blau gas. In this process the oil is decomposed in the retorts, as in the manufacture of Pintsch gas. The gas is purified and then compressed to 100 atmospheres, so that the greater portion of it liquefies. Under this pressure the liquefied hydrocarbons probably absorb and hold in solution some of the olefines and paraffines that would normally be gases at this pressure. The oil is gasified at a rather lower temperature than that ordinarily employed in the manufacture of oil gas. The fixed

gases that are left after compression are used in operating the machinery necessary in the manufacturing operations. The liquefied gas has a specific gravity referred to water of .59. The liquid is sold ordinarily in seamless steel flasks that hold 45 and 10 k.g. The gas is first expanded from 100 atmospheres down to about 10, and is then expanded again to 10 or 12 ins. water pressure. One gallon of the liquefied gas will yield about 28 cu.ft. of expanded gas. There will remain, however, a residue that may run up to 9 per cent. The following may be taken as a typical analysis of the expanded gas:

Illuminants	51.9%
CO	.1
H_2	2.7
Methane and ethane	44.1
CO_2	.0
O_2	.0
Nitrogen	1.2
Specific gravity	1.02
Heating value	1704 B.T.U.
Flat flame, calculated at 5 ft. per hr.	48.25

It will be noted that this gas is slightly higher in illuminants and heating value than the Pintsch gas, and is, therefore, slightly more concentrated. It has found some application for use in isolated localities and marine lighting.

Gasoline Gas. Gasoline gas is a mixture of atmospheric air and light hydrocarbon vapor in varied percentages generally above the explosive limit. This gas has been developed to meet the requirements of isolated localities where the quantity of gas required is small, so that the installation of the usual form of coal or water gas apparatus would not be profitable. There are two general systems used in its manufacture; one system operates in the cold while the other system employs heat to aid in the vaporization. Gasoline or carburetted air gas differs from the ordinary forms of coal gas, water gas or oil gas due to the fact that it is a simple mixture of the vapors of a liquid hydrocarbon which is not changed chemically in the vaporization. In the cold process where the air is not heated, a very light grade of gasoline must be employed, while in the system employing steam or other source of heat to assist in the evaporation the less expensive naphthas may be used.

It is essential in either process that the hydrocarbon should be entirely vaporized and should contain no traces of tar which would otherwise stop up the apparatus and give trouble in the burners. The gasoline with a sp.gr. of about .65 is usually employed in the cold system. While this leaves a small residue it is not sufficient to cause serious trouble.

The volume of vapor that can be carried by a given volume of air depends upon the temperature and rises very rapidly with increase in temperature. The data relating to this point are rather meager and frequently somewhat contradictory, but in general, the air can be depended upon to carry over 10 per cent of the vapor, even at low temperatures.

The percentage carried is important in that it must either be lower than the explosive limit, that is less than about 2 per cent, or higher, that is above 5 per cent. In this country, the usual practice is to produce a mixture containing over 5 per cent of the gasoline vapor, the mixtures averaging from $5\frac{1}{2}$ to 6 gallons of gasoline per thousand feet of the mixture. This would give a gas containing over 13 per cent of vapor, which is amply safe from explosion and which would give about 16 candle power in the Argand burner and will have a calorific value about 570 B.T.U.'s. It can therefore be employed for either lighting or heating.

During the last few years a number of systems have been exploited, using heat to assist in the vaporization of the heavier grades of naphtha. These naphthas have a gravity of from .69 to .71. These machines either use steam or a small flame fed from the machine itself. They are generally provided with automatic devices so that their operation is very simple.

The great disadvantage of these systems is the fact that the gas has a high sp.gr., about 1.26, so that in case of leak it does not rise and is thus less readily dissipated by the ordinary means of ventilation. The pipes that are used to convey it are generally of large diameter and care must be taken to prevent exposure to cold draughts, as the gasoline vapor present has a tendency to condense out at temperatures below 40° F. and should any volume of the condensate collect in the pipes it would be a source of danger, in case it passed over to the burners.

Another recent development is the use of mixtures containing less than 2 per cent of gasoline vapor that is below the explosive limit. Such mixtures although low in heating value may be used with a Welsbach mantle without further admixture of air.

Acetylene. The use of acetylene as an illuminant in small towns and for isolated plants has developed to a very considerable extent during the last five years, owing to the standardization that has taken place in the manufacture of calcium carbide, while accurate data cannot be had as to the extent of its use. Brown's Directory of Gas Companies reports 184 acetylene town plants in operation the first of this year. These works report a total output of nearly 19,000,000 feet. It is probable, however, that there are many more plants in existence which did not take the trouble to file their report. To this must be added a very large number of small private plants lighting one or more houses or a factory, and a very considerable quantity of acetylene that is used in the portable tanks for automobile headlights, etc.

Calcium carbide is manufactured in the electric furnace by fusing a mixture of lime and coke. Although acetylene was known chemically as far back as 1836, and in 1862 the formation of calcium carbide was discovered by Woehler, it was not until Wilson's discovery in 1892, that calcium carbide could be commercially manufactured in the electric furnace, that acetylene became of any importance as a possible illuminant.

In the manufacture of calcium carbide, the purity of the raw materials is of great importance and much of the success in the commercial use of acetylene can be attributed to the care taken and the chemical control exercised in the manufacture of the carbide. After fusion in the furnace, the carbide is crushed, sized and packed in hermetically sealed cans. Calcium carbide as formed in the electric furnace is a hard crystalline substance of grayish color and weighs about 138 lbs. per cubic foot.

It is usually packed in cans, holding 200 lbs. The commercial sizes for large generators are $3\frac{1}{2}$ ins. to 2 ins. and for lamps 1 in. to $\frac{1}{2}$ in. and some other smaller sizes running down to dust.

While pure carbide should yield about 5 cu.ft. of acetylene per pound, the yield of gas varies with the size. The larger lumps yield considerably more gas per pound. The British specifications provide that the standard size $2\frac{1}{2}$ ins. to 1 in. shall yield not less than 4.8 cu.ft. at 60° and 30 ins. bar. with an allowance of 5 per cent for the analysis, and that it shall not contain more than 5 per cent of dust that will pass a $\frac{1}{16}$ in. screen. The German specifications provide three grades for sizes down to $\frac{3}{5}$ in. The price shall be based on a minimum yield of 4.81 cu.ft. per pound with a 2 per cent allowance for analysis. Carbide yielding not less than 4.33 cu.ft., however, must be accepted with a proportional reduction in price. For the smaller sizes, the base yield is 4.33 cu.ft., and carbide must be accepted that does not yield less than 4.01 cu.ft. The maximum amount of phosphine present in the crude acetylene shall not exceed .04 per cent, with an allowance of .01 per cent for the analysis.

The formation of acetylene from the carbide takes place according to the following reactions:

$$CaC_2+H_2O=C_2H_2+CaO \quad \text{and} \quad CaO+H_2O=Ca(OH)_2.$$

This reaction does not takes place below $-5°$ C., however. This reaction is exothermic, but there is some disagreement as to heat of formation of the acetylene, the net result of the reaction being about 29.1 large calories. This heat of formation is really very important as it must be taken care of in a design of the generator. Acetylene polymerizes very readily at 600° C. into benzol and at higher temperatures forming other complex organic compounds. For this reason, it is essential that ample water should be present to absorb the heat of the reaction or other means must be provided to prevent an excessive rise in temperature. Experiments on the temperatures, occurring in generators, have shown

a maximum of from 280 up to as high as 807°, in one case reported by Lewes. Furthermore, at high temperatures, the acetylene may decompose violently, the critical point being about 780°. The heat set free may thus result in an explosion, while if any air is present, it may explode at 480° C. On account of these facts it is exceedingly important that well-designed generators should be used for the generation of the gas. The generators may be divided into two general classes: first, where the carbide is added to the water, second, where the water is added to the carbide. Either of these may be automatic or non-automatic. The American regulations require that the maximum rise shall not exceed 53° C., and that there shall be present at least $8\frac{1}{4}$ lbs. of water per pound of carbide, while for the hand-fed generators the rise shall not be over 91° C.

Owing to the rise of temperature in the generator, considerable water is vaporized and passes off with the gas, so that a generator requires considerably more water than is indicated by the reaction, the usual allowance being about half a gallon per pound of carbide.

Pure acetylene has a sp. gr. of .9056; its critical temperature is 37° C. and the critical pressure 68 atmos. The specific heat is .373 and its calorific value is 1440 B.T.U.'s per cubic foot. When mixed with air, it ignites at about 430° C. Its explosive limit varies from about 2.5 to 55 per cent.

At 15° C. it is soluble volume for volume in pure water, but the presence of lime or sodium salts in the water such as would exist in the generator, reduces the solubility to about one-third of this figure. Above two atmospheres pressure and at 780° C. acetylene is very unstable and is likely to decompose violently. For this reason liquefied acetylene is very dangerous and its use is generally prohibited. Various solvents such as acetone will take up large volumes of acetylene and this property is made use of in the portable tanks used for automobile headlights. The tanks are filled with a porous material, containing about 80 per cent of voids, about 43 per cent of these are filled with acetone. The acetylene is then compressed into the cylinder at a pressure of 10 atmos., at which pressure the cylinder will hold about one hundred times its volume of acetylene.

Crude acetylene, when first generated from the carbide, contains ammonia, hydrogen sulphide and phosphine, which must be removed before the gas can be used for indoor illumination. The average quantities in the crude gas are probably as follows:

Ammonia	100 to 175	grs. per 100 cu.ft.
Hydrogen sulphide	10 to 50	" "
Phosphine	20 to 40	" "

The ammonia is readily removed by the water in the holder that is usually a part of each generator, but the phosphine, which is the most

noxious impurity, must be treated chemically. Various purifying materials have been proposed, most of them based on mixtures of bleaching powder, slaked lime and some other chemical which gives them a claim for being novel. Another material which seems to have given fair success is known as heritol. It is composed of kieselguhr, saturated with an acetic or hydrochloric acid solution of chromic acid. This latter material has an advantage, due to the fact that it changes in color when saturated with the impurity.

Purified acetylene is usually burned to give a luminous flame and owing to the richness of the gas, it is necessary to employ small burners, or else make extra provision for injecting air into the body of the flame by the action of the issuing gas. A usual form of burner has two jets, which impinge and form a flat flame, thus drawing air in on all sides. To assist in the injection of the air and to overcome the high sp.gr. of the acetylene, requires a rather high pressure, considerably higher than that required for coal gas. When burned in such an open flame burner at low rates, the horizontal candle power, if computed at a rate of five feet per hour, would give from 240 to 250 candle power. Calculated on the candle power per foot per hour, it seems to give about 40 candle power. The comparatively high efficiency of the acetylene flame is due not only to its high carbon content, but also to its very high flame temperature, which results in part from the strongly endothermic nature of the gas, disengaging a large quantity of heat when it is dissociated. Mahler gives the flame temperature at 2350° C. while Le Chatelier estimates it from 2100 to 2400° C. This is reflected in the high duty obtained when acetylene is burned in a Welsbach mantle where from 120 to 140 candles per foot are obtained.

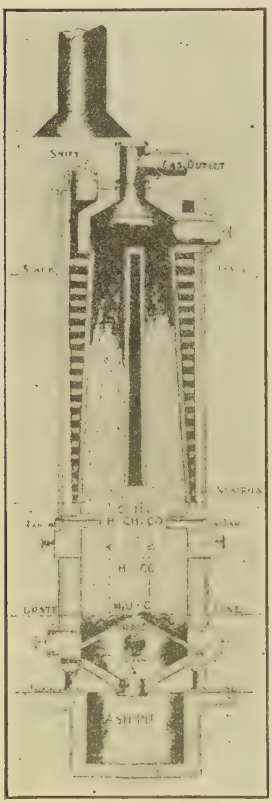


Fig. 233.—Methane-Hydrogen Generator.

Owing to the relatively high cost of the heat units in acetylene, it is not an economical fuel, but stoves are now on the market which utilize its high heating value (1400 B.T.U.'s) very efficiently and satisfactorily, and in isolated localities, where it is already employed for lighting, it may serve a very useful purpose where economy is not of prime importance.

In connection with the distribution of acetylene care must be taken to insure perfect tightness in the distributing system, owing to the high value of the gas. The use of copper wherever

the gas may come in contact with it, must be avoided, as acetylene forms a very explosive compound when brought into contact with copper. This compound is known as copper acetylide, a body to which Blochmann's formula $C_2H_2Cu_2O$ is generally ascribed.

During the past few years there has been a tremendous increase in the use of acetylene and oxygen for the autogenous welding of steel aluminum, etc., for making repairs and for cutting large steel sections.

Methane-Hydrogen Gas. There are a number of special processes which have been developed to furnish gas either from by-products or for special purposes; among these is the so-called methane-hydrogen gas, which was designed to utilize tar. The cross-section of the generator, Fig. 233, is shown in the cut. The tar is sprayed into the combustion chamber, where it is vaporized, and then passes through the bed of fuel, which is raised to incandescence by an air blast. In contact with the carbon, the ring compounds from the tar are decomposed. The principal product is hydrogen, together with 10 or 15 per cent of methane, carbon monoxide and a small percentage of illuminants. While the illuminating value of the gas is low, it can be readily enriched with benzol, if required, and furnishes a commercial solution for the gasification of tar or the manufacture of a low grade of gas. Analyses of this gas show about the following composition:

Illuminants	3	per cent.
Carbon monoxide	15	"
Hydrogen	64.2	"
CH_4	12	"
C_2H_6	0	"
CO_2	2.3	"
Oxygen	.2	"
Nitrogen	3	"
Candle power	11	"
B.T.U.	400.[1]	"

The same principle is utilized in the Rincker and Wolter system, which was designed to utilize tar and heavy oil residues which could not be handled in the ordinary carburetted water gas apparatus. A mixture of two parts of oil residue and one part of water gas tar is sprayed downward on the bed of heated fuel, decomposing the hydrocarbons. The free carbon, which is liberated, settles on the coke and is burned during blasting. They claim a composition as follows:

Illuminants	8.8	per cent.
CO	3.3	"
H_2	59.2	"
CH_4	17.9	"
CO_2	1.0	"
Oxygen	.3	"
Nitrogen	9.5	"

The calorific value may be varied between 350 and 650 B.T.U.'s. A mixture of equal parts of coal tar, water gas tar and Java residue would yield about 20,000 ft. per ton of 500 B.T.U. gas. This process can be varied so that the more complete decomposition is secured and a high yield of hydrogen obtained, thus making a gas suitable for balloon purposes.

Balloon Gas. Within the past few years due to the increased use of both dirigible and captive balloons, especially for military purposes, there has existed a very great demand for suitable inflating gases. Such a gas should have a low gravity so as to have a minimum lifting power of about 43.6 lbs. per thousand cubic feet. This would correspond to a gravity of .43. Apparently, a gravity of about .33 is considered the most efficient, owing probably to the greater loss by diffusion through the fabric if lighter gravities were used. A number of processes have been devised to prepare suitable gases with the ordinary manufacturing apparatus. Such a process has been patented where the standard form of carburetted water gas apparatus is used. In carrying out this process the fire is carried low, and just enough steam is admitted to prevent burning out the grate bars and to keep down clinker. After the fire has been brought to a working temperature with the blast, from 15 to 20 per cent of the oil is admitted to the top of the fire. This purges the set of the heavy products of combustion. The stack-valve is then closed and the remainder of the oil admitted. The valves are reversed and a small amount of steam is turned on under the fire, which passing up through the fuel bed generates water gas, clears the machine of the oil gas and is used to reduce the gravity to the point desired. The oil, partially decomposed in the fuel bed is completely decomposed in the fixing chambers, due to their very high temperature. In this way the illuminants which have an injurious action on the rubberized fabric are practically eliminated, and by suitably varying the amount of steam any desired gravity may be made. Two analyses of this gas show the possibility of varying the gravity:

Illuminants	1	and .4	per cent.
CO	15.3	" 5.2	"
Hydrogen	63.7	" 75.4	"
Methane	11.0	" 10.4	"
Ethane	.8	" .0	"
Carbon dioxide	2.6	" 1.0	"
Oxygen	.5	" .6	"
Nitrogen	5.1	" 7.0	"
Specific gravity	.37	" .35	"

Another process for manufacturing a very low gravity gas depends on the decomposition of ordinary coal gas by passing it through hot coke in a retort. The retort is raised to a temperature of about 2200° F. A 10-ft. retort will produce about 300 cu.ft. of gas per hour, the gravity

depending somewhat upon the quality of the coal gas, ranging from .22 to .3. Its analysis is about as follows:

Illuminants	nil
CO	7.3 per cent.
Hydrogen	80.7 "
Methane	6.9 "
CO_2	nil
O_2	nil
Nitrogen	5.1 "

The Messerschmidt process is used quite extensively abroad for the production of hydrogen for military purposes. This depends upon the decomposition of steam by metallic iron and the reduction of the iron oxide by blue water gas a mixture of carbon monoxide and hydrogen, produced in a separate apparatus.

The hydrogen generator is shown diagrammatically in Fig. 234.

The iron mass is introduced into the cylindrical iron retort formed by the concentric iron cylinders *A* through the filling doors *F* and *F'*; it may be removed for replacement through the doors *G* and *G'*. In order to heat the apparatus and reduce the iron oxide to metallic iron, blue gas made in a separate generator by the decomposition of steam by incandescent coke is introduced at the base of the inner cylinder at *B*, and partially burned in contact with the checker brick filling, by air introduced at *C*. This combustion serves to raise the temperature of the iron oxide to a point at which the unburned CO and H_2 of the blue gas in passing down through the heated oxide will react and reduce the oxide. The products pass upwards again around the iron retort and any unburned gas is consumed with auxiliary supplies of air introduced through *D*1, *D*2, *D*3, *D*4; this heats the firebrick lining of the shell and equalizes the temperature in the apparatus.

The products of combustion pass out through the flues *H*, the pipe *I*, the stack valve *J*, to the stack *K*. When the temperature of the mass has been raised to 700°–800° C. and the iron is reduced to the metallic state, in accordance with reaction $2FeO+CO+H_2=2Fe+CO_2+H_2O$, the blue gas and air is shut off and a small amount of steam is turned on at *P* to purge the apparatus, when hydrogen appears at the stack valve the valve is closed and the steam shut off at *P* and is turned on at *O*. The steam in passing around the outer passage is superheated and in passing up through the heated iron is reduced with the formation of hydrogen in accordance with $Fe+H_2O=FeO+H_2$.

The hydrogen passes out through the pipe *L* to the water seal *M* and through the pipe *N* to the purifying apparatus. The heating and reduction stage require about twenty minutes, the generation of hydrogen about fifteen minutes. The cycle is then continued. The temperature is con-

trolled with pyrometers and the large mass of checker brick in the inner cylinder and the heavy firebrick lining of the shell serve as a heat storage.

The hydrogen is cooled and freed from dust by washing with a water spray, CO_2 is removed with lime and H_2S with iron oxide.

The purity of the hydrogen is claimed to exceed 99 per cent.

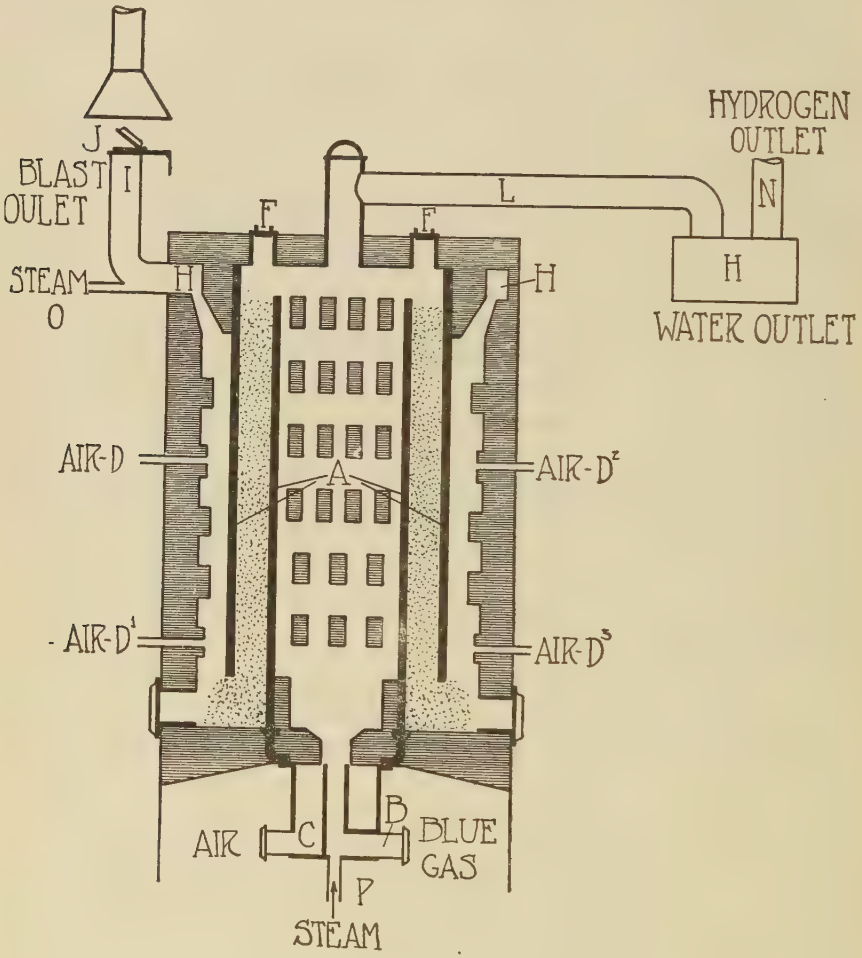


Fig. 234.—Messerschmidt Hydrogen Generator.

Utilization of Residuals. The residuals or by-products depend upon the kind of gas made. Coal gas gives coke, coal tar, ammonia, cyanogen, spent oxide and retort carbon. Water gas has only one, the tar, while the all-oil gas of the Pacific Coast yields lampblack. Pintsch gas furnishes a small quantity of tar and condensate that is separated during the compression.

The retort coke is usually crushed, the breeze or fine dust removed and the crushed product separated into several sizes for sale. The breeze

is usually burned at the plant as boiler fuel either alone on specially constructed grates with forced draft or mixed with coal, or sold as filtering material. The greater portion of the coke is used by bakers or for other purposes where a quick high heat is required. Owing to its small size, high sulphur and volatile content and low crushing strength it has not been used for foundry purposes to any great extent.

The lampblack is allowed to drain and air dry and may be used directly as boiler fuel, but successful results have lately been obtained by briquetting the dried material, there being sufficient tar present to act as a binder.

The retort carbon is sold as such and is used in the manufacture of arc and battery carbons, dry batteries and other purposes requiring a hard, dense form of carbon.

The various tars are generally sold to tar distillers after removing as much as possible of the water with which they are always mixed in the process of recovery, only a few of the larger works attempting to refine their tar. In many of the smaller plants and where freight rates are unfavorable or other conditions do not admit shipping the crude tar to a distiller, the tar is burned as fuel under the benches or boilers. The tars will range from 15,000 to 18,000 B.T.U. in heating value per pound.

The Recovery of Crude Benzols. The enormous and insistent demand for benzol and toluol as raw materials for the manufacture of explosives during the past three years has resulted in a great increase in the recovery of these products from both coke oven and illuminating gas.

The following figures give an idea of the estimated increase in the production of benzol and toluol during the last four years:

	1913 Gallons.	1915 Gallons.	1917 Gallons.
Benzol.....	4,000,000	8,500,000	30,000,000
Toluol.....	850,000	2,500,000	12,000,000

While the recovery of crude benzol from by-product ovens has been a standard practice for many years yet it is only within the past three years that commercial conditions have been such that this could be done with illuminating gas.

This has been due to the fact that until very recently the greater part of the illuminating gas was produced under regulations requiring a high illuminating value and that in removing the crude benzol from say a coal gas; the illuminating value would be reduced from 12 to 13 candle-power to 3 or 4, or a decrease of 68 per cent; the heating value would be reduced from 610 B.T.U. to 570 B.T.U., or only 6.5 per cent.

In the summer of 1917 some dozen plants were in operation recovering toluol from both coal and carburetted water gas, while it is highly probable that within another six months all of the larger gas plants will have installed recovery apparatus.

The amounts and relative proportions of the condensible hydrocarbons

present in illuminating gas varies considerably with the process, i.e., coal-carburetted water gas, all-oil water gas; and with the type of apparatus; and with the raw materials.

In discussing the quantities involved it has been thought more logical to express them in gallons per ton of coal carbonized for coal gas and as a percentage of the gas oil used for carburetted water gas.

	Horizontal Retorts.	Vertical Retorts.	Coke Ovens.	Carb. Water Gas.	All-oil Water Gas.
				Per cent.	Per cent.
C.P. benzol	1.62	1.81	1.782	4.5	3.3
C.P. toluol	.41	.43	.402	2.2	.2
Refined naphthas	.30	.41	.216	1.0	.03
Unsaturated hydrocarbons	.36	.43	.297	3.1	.60
	2.69	3.08	2.707	10.8	4.13

In this connection the use of " C.P." and " refined " indicates that the hydrocarbons were washed with acid and soda before valuation.

In 1915 a process known as the " C " process was used to recover benzol and toluol from coal gas. This consisted in bringing the gas in contact with the coal tar, the latter absorbing a certain amount of the light hydrocarbons, thus yielding a light oil richer in benzol-toluol. The process, while rather simple in application, is not very efficient in that it would recover only from 10 to 15 per cent of the benzol and from 25 to 40 per cent of the toluol present in the gas, while it involved distilling a large amount of coal tar to recover the small amount, say not 5 to 6 per cent, of benzol and toluol content.

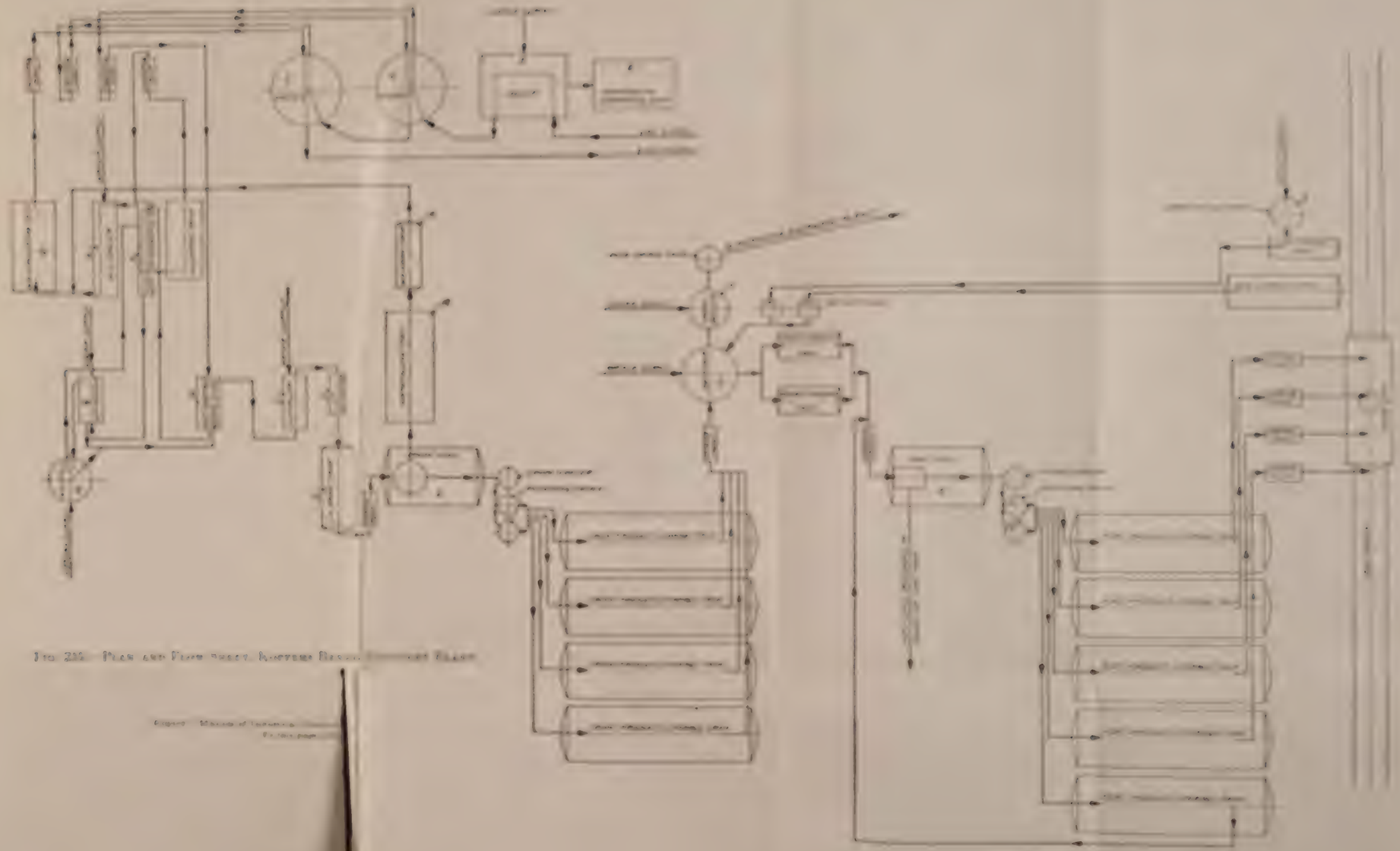
The method of recovery in general use involves scrubbing or washing the gas with an oil of high boiling-point (low-vapor tension) until it has absorbed from 2.5–3.0 per cent of the light hydrocarbons, the so-called benzolized oil is then heated to 240° to 280° F. and distilled with live steam, thus liberating the low-boiling benzol homologs. The debenzolized wash oil is then cooled by heat-exchanging apparatus and water coolers and is returned to the cycle.

It is evident that given a wash oil of low vapor tension the extraction will depend upon the relative amount of low-boiling vapors present, the saturation of the benzolized wash oil, i.e., the volume of wash oil per unit volume of gas, and the temperature.

As the temperature increases the volume of wash oil must be increased to decrease the percentage of saturation to obtain equal efficiency of extraction.

The highest commercial efficiency of extraction is between 92 to 95 per cent, while average working will probably not exceed 90 per cent.

From some work done on carbonated water gas the following table gives the relative amounts of wash oil required with the gas at varying temperatures for the extraction 96 per cent of the toluene present:



Temperature of Gas, ° F.	Relative Quantity of Oil Required. Gallons per 1000 cu. ft.
70	4.0
80	6.2
90	8.0
100	9.1
110	10.1

In this connection it should be remembered that the efficiency of extraction will vary with the different hydrocarbons, as at somewhat elevated temperatures it is possible to secure a relatively high extraction of toluol where this is the product desired, while the extraction of benzol will be considerably lower.

Some typical experiments give the following results:

	Inlet Gas. Gallons per M.	Outlet Gas. Gallons per M.	Extraction. Per Cent.
Benzene	.199	.104	47.5
Toluene	.101	.007	93.1

The wash oil used is generally a high-boiling petroleum oil known as "absorbent" or "straw oil." The following specifications will furnish a very satisfactory material:

Gravity at 60° F., 34° to 36° B.
Flash-point open cup not less than 275° F.
Viscosity Saybolt at 100° F. not over 70.
Pour test not over 30° F.
Steam distillation not over 1 per cent.
Loss on washing with 100 per cent H_2SO_4 not over 10 per cent.

In England creosote oil is used to some extent; it should have a gravity at 60° F. of 1.04 and at least 90 per cent should distill between 200° and 300° C.

The oil should not contain over 5 per cent naphthalene.

The petroleum oils are generally more satisfactory, as they are less likely to form emulsions with water and they appear to give up the absorbed light oils more readily in the steam distillation.

The recovery apparatus is usually installed in coal-gas plants after the ammonia washers where the gas has already been cooled and the temperature for the highest extraction is rarely allowed to exceed 75° F. In water-gas plants it is usually installed after the purifiers.

While the main features of the recovery apparatus is the same in nearly all the modern systems there are a number of minor points of difference, principally in design.

As an example, for illustration, a Koppers recovery plant is illustrated in Fig. 235, while Figs. 236 and 237 give some views of apparatus installed.

Here the gas is brought into contact with the wash oil in two tall towers

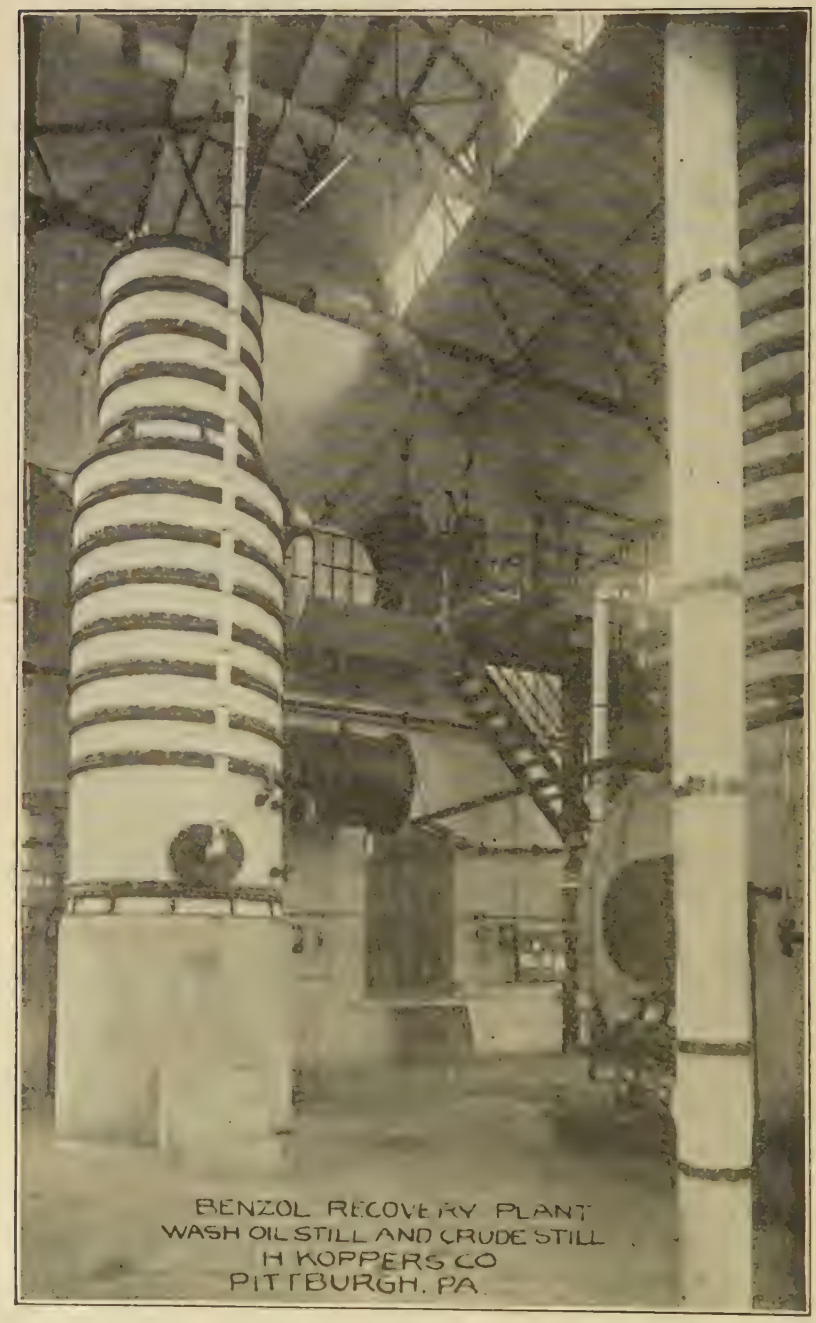

BENZOL RECOVERY PLANT
WASH OIL STILL AND CRUDE STILL
H KOPPERS CO
PITTBURGH. PA

Fig. 236.

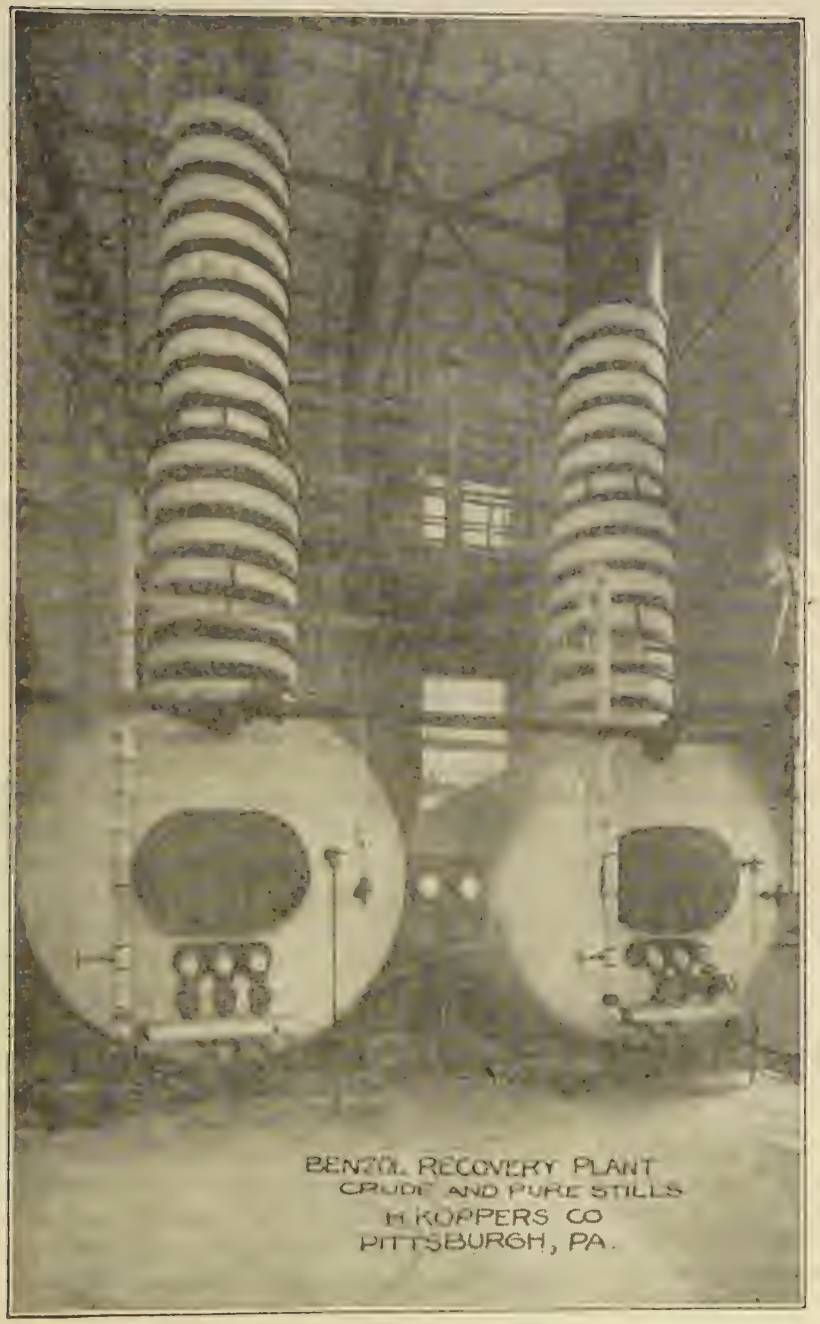

BENZOL RECOVERY PLANT
CRUDE AND PURE STILLS
H KOPPERS CO
PITTSBURGH, PA.

Fig 237.

filled with layers of boards on edge in order to break up the gas stream and to expose the maximum surface of oil to the gas. The oil is sprayed down the towers against the rising stream of gas. Separators similar to steam separators in the gas outlet pipes prevent the loss of wash oil in the form of the mist or spray while the bottom of the towers and external separators similar to Fig. 215 remove any water that is deposited out from the gas. The wash oil now contains from 2.5 to 3.0 per cent of crude benzol and is at a temperature of say 75° F.

It then passes to a vapor to oil heat exchanger where it is heated to 150° F. by the latent heat of the vapors from the debenzolizing still, then through an oil to oil heat exchanger where it is heated to 220° F. by the hot wash oil from the bottom of the still, hence to the steam preheater where high-pressure steam is used to bring the temperatures up to 270° to 290° F.

It is essential that the oil be brought to a high temperature before it enters the still. The hot oil now passes down the column of the debenzolizing still. This is composed of cast-iron sections of the same general principle as that shown in detail in Fig. 236, but having somewhat larger run-back passages.

Usually there are 8 or 10 sections at the top of the column of a smaller sectional area than the 14 to 18 sections at the bottom through which the oil flows. At the base of the column is a spray through which live steam is introduced in amount equal to 70 to 100 per cent of the volume of crude benzols distilled out.

As the steam rises through the current of descending hot oil the low-boiling vapors in conformity with well-known physical laws are liberated and rise through the column, thus thoroughly scrubbing the incoming oil and depositing in the upper sections the considerable quantity of the wash oil that is carried forward mechanically. A certain amount of the wash oil, however, comes over with the crude benzols and may run as high as 20 per cent by volume, although good working condition will reduce this to from 3 to 8 per cent.

The vapors then pass to the vapor oil heat exchanger, where they give up most of their latent heat to the incoming benzolized wash oil, then to condensers, and finally to a separator to remove the condensed steam and to the storage tanks.

The debenzolized wash oil leaves the base of the column at about 240°F. and passes through the oil to oil heat exchanger, thus heating the incoming benzolized wash oil and cooling to about 170° F.; from here it passes to the coolers which are usually of the ammonia type where it is cooled to 75° F., and then passes to the debenzolized wash oil tank and is ready to commence the cycle again.

In other systems the tower scrubbers are replaced with mechanical scrubbers, or in one system with a column similar to that used in the debenzolizing still.

In the various forms of heat exchangers there is a considerable diversity in design, as the amount of heat put into the oil is rather large and theoretically, since all the products except the live steam pass through a complete cycle, it should be nearly all recoverable. Considerable care has been used in an endeavor to reduce the steam and water required to a minimum.

The rate of heat transmission between oil and oil is rather low, so that skillful design is required to avoid the use of excessive areas of transmitting surface.

There are a number of variations in the design of the debenzolizing columns, but these are principally in the shape and distribution of the vapor caps and in the location of the liquid run backs.

The oil coolers are usually of the well-known ammonia type.

The oil superheaters vary considerably from the straight-tube condenser type with the steam in the tubes to modifications of the feed-water heater with coiled tubes and the steam passing around the tubes. On account of the viscosity of the scrubbing oil and the evolution of considerable vapor it is not considered the best practice to pass the oil through the tubes.

In some of the smaller plants the usual type of solid plunger steam reciprocating pump is used, but in the larger plants rotary pumps either with individual electric drive or belted to a common counter shaft to insure relative uniformity of operation are generally used.

In the operation of recovery apparatus the quantity of recoverable hydrocarbons present, the gas temperature and the efficiency of recovery desired are determining factors.

In coke-oven plants where complete recovery is aimed at the temperatures are usually held below 75° C., and sufficient wash oil to yield saturation of the benzolized oil of not over $2\frac{1}{2}$ per cent, i.e., at 2.0 gallons of light oil per ton of coal and 10.800 cu.ft. per ton this would mean 7.22 gallons of wash oil per 1000 cu.ft. with higher temperatures and greater quantities of light oils present, the wash oil used may run up to 14 to 16 gallons per 1000 cu.ft. In scrubbing illuminating gas for the primary purpose of removing toluol much higher saturations of the wash oil are used, as this while it decreases the efficiency of benzol removal does not affect the toluol removal seriously and greatly decreases the amount of wash oil required for circulation with the resulting decreased consumption of steam power and cooling water.

The practically complete elimination of the light oil from the benzolized oil is important in securing high recovery efficiencies. To a great extent this is secured by a uniformly high temperature of the oil entering the debenzolizing column. It is difficult to secure complete elimination of light oil with a temperature less than 220° F., and this will require considerably more live steam than where the oil is from 240° to 280° F., at the temperatures the recovery is complete and the whole operation is much more smooth and uniform. The live steam required varies from 70 to 100 per cent by volume of the light oil produced.

Some typical analysis of light oil from different gases are as follows:

	Horizontal Retort Coal Gas. Per Cent.	Coke Oven. Per Cent.	Water Gas. Per Cent.
Benzene	55	60	40
Toluene	15	14	21
Solvent naphtha	12	8	9
Other Hydrocarbons	13	10	27
Wash oil	5	8	3

The percentage of wash oil carried over with the light oil will depend upon whether a dephlegmator is used on the debenzolizing still and upon the amount of live steam used. With a normal amount of live steam and a dephlegmator it can be held down to from 2 to 5 per cent while without a dephlegmator and excessive steam it may rise to 12 to 15 per cent or even higher.

In the majority of recovery plants the light oil is sold as such to refining plants where it is worked up for benzol, toluol, solvent naphtha, etc., as described in Chapter XXI. In some of the larger plants recovering light oil from illuminating gas the light oil is fractionated in a steam column still similar to that shown in Fig. 242, Chapter XXI, into a crude benzol, a crude toluol, a crude solvent fraction and the wash oil recovered and returned to the system.

Some typical analyses of these crude fractions would be as follows:

	Crude Benzol. Per Cent.	Crude Toluol. Per Cent.	Crude Solvent.	Residue Oil.
Benzol	75.5	3.5	.0	.03
Toluol	2.2	81.2	3.9	.04
Naphthas	.6	3.9	39.5	.11
Residues	2.0	1.9	15.4	99.64
Wash loss	18.7	7.6	43.0	.13
Distillation loss	1.0	1.8	1.2	.05

The crude benzol may be returned to the gas vaporizing it with steam where the illuminating standard is in force. The crude toluol is sold as such and the crude solvent may be sold or in the case of carburetted water gas plants it may be used in the apparatus in place of gas oil. With proper heat control a large proportion of the solvent naphtha is converted into toluene which is subsequently recovered.

The refined benzol and toluene produced from light oil recovered from coke oven gas is practically free from paraffin hydrocarbons, but where the light oil is recovered from illuminating gas under certain conditions considerable quantities of paraffin or cyclical paraffin hydrocarbon may be present in the refined toluene, the benzol apparently being practically free.

This formation of a paraffin of a low gravity is apparently due to certain coals and oils and to the heat treatment they are subjected to.

In horizontal retorts practically no trouble is found except where cannel coal is used as an enricher although the crude light oil may contain as much as 2 per cent paraffin hydrocarbon.

In vertical retorts practically when completely filled the light oil may contain as high as 13 per cent of paraffin hydrocarbons. Experiments have indicated that this can be reduced by lowering the charges and increasing the carbonizing temperatures.

With carburetted water gas certain oils give practically no trouble under ordinary operating conditions while other oils require an increased fixing temperature (from 100° to 150° F.) to reduce the paraffin content to a point where it will not give trouble in nitration.

There are certain oils, however, that do not seem to yield to any commercially practicable variation in the heat treatment, and will yield refined toluene, boiling within less than 2° F., that will contain as high as 5 per cent of unnitrifiable hydrocarbons.

These are shown by the abnormally low specific gravity. A pure toluene will have a specific gravity at 60° F. of about .8710.

These non-nitrifiable hydrocarbons have a gravity ranging from .71 to .75 so that their presence is readily detected by low specific gravity, as, for instance, a toluene having a specific gravity of .864 would contain approximately 5 per cent of non-nitrifiable or paraffin hydrocarbons.

Investigation of these hydrocarbons has indicated that they are probably a mixture of octanes and nonanes with some cyclical paraffins which seem to form constant boiling mixtures with toluene.

Owing to the small amount of cyanogen present in coal gas and the variation and technical control involved in the operation of recovery plants but few gas plants have installed a recovery plant for cyanogen compounds. There are several processes in use. One involves scrubbing the gas after the removal of the tar and naphthalene with a sludge of ferrous carbonate in a solution of soda ash this yields a crude solution of sodium ferrous cyanide and ammonia, that is usually sold in the crude state and the formed solution containing $\frac{3}{4}$ to 1 lb. of ferro cyanide of sodium per gallon.

Another system involves washing the gas with ammonia liquor containing sulphur, this forms an ammonium polysulphide which reacts with the gas to form ammonia sulpho cyanide. This method has been modified by Williams within the last few years. The gas is scrubbed in ordinary cast-iron purifying boxes filled with spent oxide, which furnishes the necessary sulphur, and a strong ammonia liquor is sprayed over the oxide to keep it well saturated. This system is claimed to give a very high percentage of extraction—from 90 to 95 per cent, and produces a solution carrying about 2 lbs. of ammonia sulpho cyanide and 6 per cent of ammonia. These systems, while they are quite generally used in England, have not been generally adopted here.

Two of the largest plants in this country practicing cyanogen recovery use the system in which the gas is scrubbed before the removal of ammonia with a solution of ferrous sulphate. The ammonia and hydrogen sulphide of the gas form ferrous sulphide and ammonium sulphate; this reacts with a further portion of the ammonia and the cyanogen, forming an insoluble double ferro cyanide of ammonia and iron $(NH_4)_2Fe_2(CN)_6$. A portion of this salt, however, is partially decomposed by the ammonia and H_2S in the gas into ammonium ferro cyanide and ferro sulphide.

Fig. 238 gives an outline of this process.

The mud which is formed in the reaction is boiled, which converts the soluble ferro cyanide in the presence of ferrous sulphide into the insoluble double salt. This is then neutralized with sulphuric acid and filtered. The resulting sludge or mud is sold as such to the manufacturers of cyanide compounds and the ammonium sulphate solution is evaporated to crystallization.

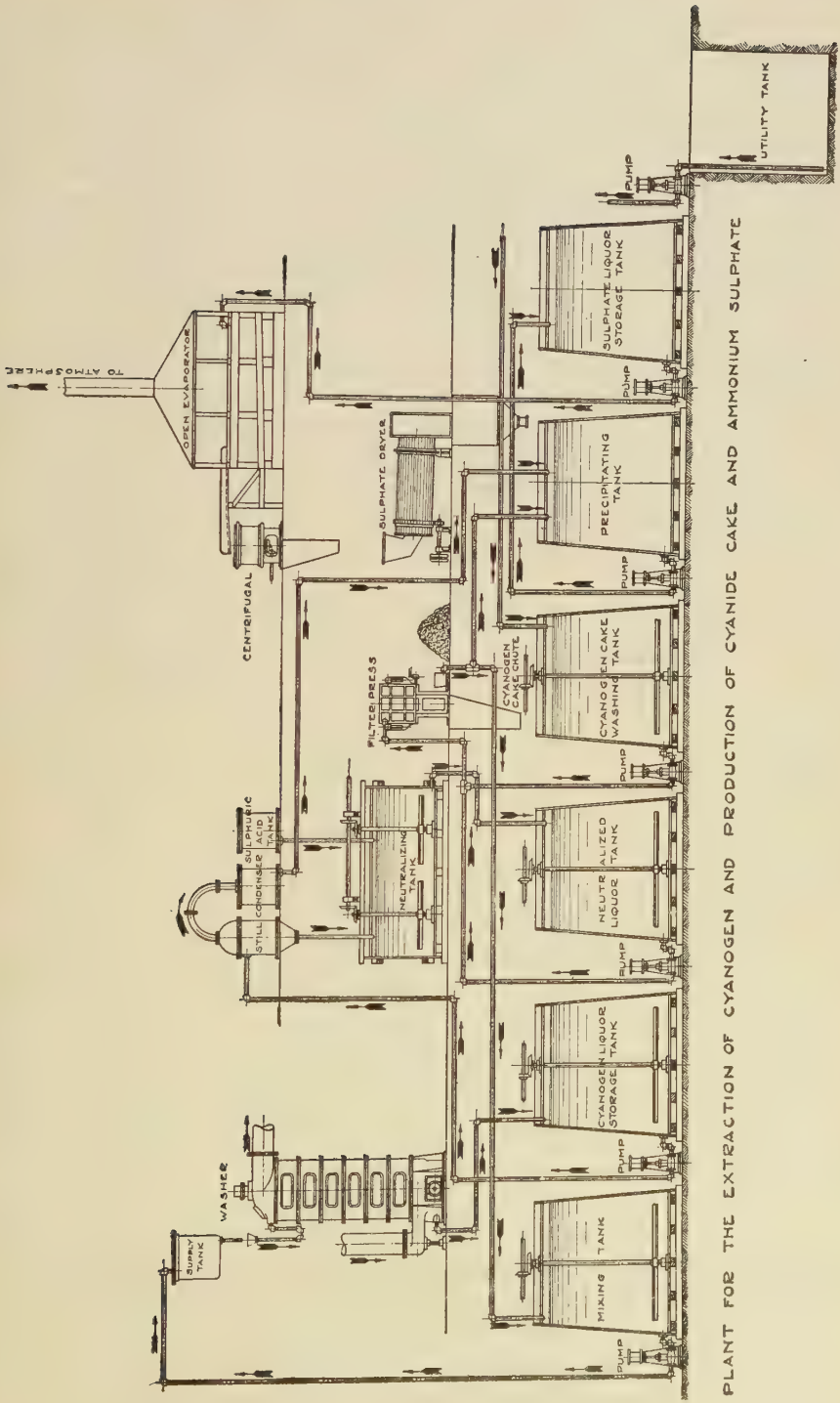
In the practical operation of the plant the gas is scrubbed with a rotary or Feld type washer with a copperas solution of about 27 per cent. The mud or sludge as it passes from the scrubber has a specific gravity about 1.2 per cent, contains about 5 per cent of cyanogen and $6\frac{1}{2}$ per cent of ammonia. The sludge is then heated in a small still to drive off a position of the ammonia which is recovered as strong ammonia liquor, and it then passes through the lead-lined neutralization tanks provided with agitators where it is neutralized with sulphuric acid and heated just short of boiling. A slight excess of acid is carried and the neutralized solution is tested for the presence of ferro cyanide. If this is shown to be present copperas is added to precipitate it. The neutralized sludge is now pumped into the filter press, and the bulk of the ammonium sulphate recovered.

This preliminary cake is then broken up and washed with water in a tank and again filter pressed, yielding the finished cake, having about the following composition:

Moisture	50%
Insoluble double ammonium ferro cyanide	37
Tar, naphthalene, sulphur	1
Ammonium sulphate	9
Iron sulphate	1.4
Undetermined	1

The solution of ammonium sulphate is treated with strong ammonia liquor to precipitate the excess iron, after saturation and filtration is evaporated and is steam heated in lead evaporators, the ammonium sulphate crystallizes out and is freed from the bulk of the moisture in a centrifugal, and dried in a small rotary drier. A typical analysis of the sulphate:

Ammonia	25.3%
Moisture	0.3%
Freed acid	.08%



PLANT FOR THE EXTRACTION OF CYANOGEN AND PRODUCTION OF CYANIDE CAKE AND AMMONIUM SULPHATE

FIG. 238.

The operation of the plant requires considerable technical control as the quantity of cyanogen in the gas varies considerably from time to time. Tests indicating from 110 grains to 140 grains. To some extent this is influenced by the temperature used in condensation, as with the lower temperatures the greater amount of ammonia liquor condenses which takes out some of the cyanogen. The yield of cyanogen calculated as Prussian blue varies from 2.2 to 2.8 lbs. per ton of coal and the ammonium sulphate from 3.0 to 3.6 per ton. In connection with the operation of the plant it appears that the total yield of ammonia is somewhat less than where all of the ammonia is extracted as liquor. This is not surprising considering the necessary handling.

The ammonia which is recovered as condensate and as a weak liquor in the ammonia scrubbers will average from 1 to 2 per cent by weight and exists principally as an acid carbonate and chloride together with small quantities of a number of other ammonia compounds.

The following analyses will indicate the composition of several samples of ammonia liquor:

ANALYSES OF CONCENTRATED AMMONIA LIQUOR

Total Ammonia.	Horizontal Retorts. 16.35 Per Cent.	Vertical Retorts. 14.55 Per Cent.
	Per Cent by Weight.	Per Cent by Weight.
NH_4HS	1.84	3.23
$(NH_4)_2CO$	29.50	30.30
NH_4Cl	10.72	5.30
NH_4CNS	1.36	.44
$(NH_4)_2SO_4$	.14	.15
$(NH_4)_2S_2O_3$	2.10	.37
$(NH_4)_2FeCy_6$	.55	.14

In many plants the weak liquor is sold as such to manufacturers of ammonium products, but in order to make the material more convenient to handle and to save storage space and save freight, the weak liquor is generally concentrated up to a strength of from 10 to 15 per cent. This is done in ammonia stills. These consist essentially of the free ammonium still where the liquor freed from volatile salts is treated with milk of lime and the heating continued to eliminate the last traces of fixed ammonium compounds.

The ammonia gas and steam is driven off through the towers somewhat similar to the dephlegmator towers in use in the distillation of benzol, etc., and then passes to a water-cooled condenser where the concentrated ammonia is collected. In the practical operation of the plant the liquor is analyzed for the proportion of free and fixed salts and whether a proper amount of milk of lime is added. Considerable care and experience are necessary in the operation of the stills in order to insure that all of the

ammonia is driven out and this involves daily analyses of the waste liquor from the stills.

The manufacture of ammonia sulphate by the direct process has already been touched on. In the indirect process the operation is practically a combination of the concentrating apparatus as far as the stills are concerned where the liquor is freed from the ammonia the vapors instead of being condensed to a concentrated liquor are passed into the lead-lined saturator box where they are brought in contact with the sulphuric acid.

The ammonium sulphate as it forms in the saturator is fished out, allowed to drain, and is usually freed from excess moisture in the centrifugal. The manufacture of ammonium sulphate is confined almost entirely to the coke ovens.

The spent oxide from coal gas plants where the cyanogen is not extracted will contain practically all the cyanogen from the gas as Prussian blue together with some ammonium salts. In the ordinary oxide the Prussian blue will range from 7 to 13 per cent; it thus becomes available as a source of cyanogen and is sold as such. The presence of the tar, which is always present, has so far prevented the commercial recovery of the sulphur for use in the manufacture of sulphuric acid.

The further utilization of the tar is taken up in another chapter and the ammonia and cyanogen under "Commercial Chemicals," to which reference is made.

CHAPTER XXI

COAL TAR AND ITS DISTILLATION PRODUCTS

F. E. DODGE,

The Barrett Co., New York

Coal Tar. This is the black, foul-smelling, oily mixture which separates from the gases formed in the destructive distillation of coal. The raw tar is composed of light oils, pyridine bases, phenols, naphthalene, anthracene, heavy oils, pitch, complex organic compounds insoluble in benzene, and known as free carbon, water, ammonia, and dissolved constituents of the gas. As there is little prospect that the principal object of the destructive distillation of coal will be the production of tar, there has been little research upon the conditions necessary to produce tars of the most desirable properties. It varies greatly in composition and may be divided into retort gas tar and oven gas tar, according to its method of production.

Mr. Lewis T. Wright, F.C.S., has made some study of the effect of variations in the carbonizing temperature upon a caking coal in ordinary gas retorts and gives the following interesting table of the results:

	600° C	650° C	700° C	750° C	800° C
Cubic feet of gas per ton of coal	6,600	7,200	8,900	10,162	11,700
Specific gravity of the tar	1.086	1.120	1.140	1.154	1.206
Composition of the tar percentage by weight:					
Ammonia liquor	1.20	1.03	1.04	1.05	0.383
Crude naphtha	9.17	9.65	3.73	3.45	0.995
Light oil	10.50	7.46	4.47	2.59	0.567
Creosote oil	26.45	25.83	27.29	27.33	19.440
Anthracite oil	20.32	15.57	18.13	13.77	12.280
Pitch	28.89	36.80	41.80	47.67	64.080
Total	96.53	96.34	96.46	95.86	97.745

This shows not only the increased yield of gas with the increase in temperature but also the loss of the valuable light constituents of the tar and the increase in bitumens.

At 600° C. the composition of the tar approximates that obtained from by-product coke ovens and at 800° C. that obtained in modern retort house practice.

Retort Gas Tar. This tar is obtained as a condensation product in the hydraulic mains, scrubbers, or condensers, in the manufacture of coal gas for illuminating purposes. It is less fluid and contains less of the lighter hydrocarbons, more naphthalene, anthracene and their accompanying oils, and more free carbon than tars from some other sources. The composition varies with the heats and coals employed. The lower the carbonization temperature of any coal the more fluid the tar and the lower the free carbon content.

The specific gravity of the dry (water-free) tar varies from 1.10 to 1.25 or even somewhat higher.

It contains from 18 to 40 per cent of free carbon and yields on distillation from 1 to 5 per cent of light oil to about 200° C., 30 to 50 per cent heavy oil, including naphthalene, anthracene, phenols, and accompanying oils, from 200° C. to the coking temperature, and from 45 to 65 per cent coke; or if distilled to pitch the yield would be light oil 1 to 5 per cent, heavy oil 25 to 40 per cent, and pitch 50 to 75 per cent.

Oven Gas Tar. This material is obtained as a by-product in the distillation of coal in retort coke ovens. It is similar to retort gas tar, except that it is more fluid. It contains more of the hydrocarbons, and considerably less free carbon, which latter usually runs from 5 to 20 per cent.

The composition of course changes with the coal, with type of oven, and with the coking temperature.

Producer Gas Tar. Owing to the method of production usually consists of large percentages of water and free carbon together with a very small amount of oils and yields, when distilled a very friable pitch entirely unsuitable for the purposes for which pitch is made and therefore of no commercial importance.

Blast Furnace Tar. Is essentially a low heat tar, being produced in blast furnaces fed with coal instead of coke and the gases liberated from the coal come in contact with a cooler zone as soon as formed. It usually has a specific gravity between 0.94 and 1.000 and contains more phenoloid and basic substances than ordinary coal tar. These phenoloid substances resemble those obtained from the destructive distillation of wood and lignite and amount to from 5 to 10 per cent of the tar, while 1 to 2 per cent is the usual amount in ordinary coal tar.

It also contains from 2 to 5 per cent of basic bodies and about 16 per cent of paraffin oils which solidify on cooling. These tars are entirely different from the ordinary coal tar and not suited for the same purposes.

Water Gas Tar. From the manufacture of carburetted water gas for illuminating purposes, the tar obtained differs mainly from coal tar

in the entire absence of tar acids (the phenol group), ammoniacal liquor, and in the small amount of free carbon present, which is usually less than 2 per cent in these tars.

The specific gravity varies from 1.005 to 1.15, but is usually between 1.03 and 1.12 in tars from the larger and more carefully supervised works.

Dry water gas tar, when distilled, yields from 5 to 15 per cent of light oil to 200° C., 30 to 50 per cent of heavy oil from 200° C. to pitch, and 35 to 60 per cent of pitch.

Pintsch or Oil Gas Tar. This comes from the manufacture of oil gas used for railway lighting. It is similar to water gas tar, but sometimes contains much larger amounts of free carbon, frequently 25 to 30 per cent, or even more.

Application of Tar. Tar is little used in the crude state, but is refined by removing the water and more or less oil by distillation. In this

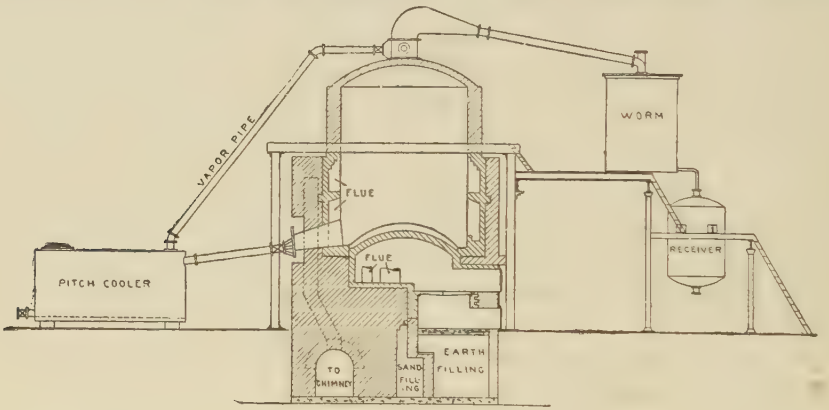


Fig. 239.—European Tar Still.

condition it is used to saturate roofing felt, to coat roofs laid with plain tar felt, as a cheap paint, and to coat wood which is to be buried in the ground. With more oil removed it is used as a binder in asphalt pavements and tar-macadam roads. With an admixture of water, it is used to sprinkle Telford and Macadam roads to prevent dust.

Tars are separated into their valuable constituents by distillation. The stills, Figs. 239 and 240, may be either horizontal or vertical cylinders set in brick work and heated by direct fire similar to steam boilers. Stills vary in size and in design. Those with a capacity of 10,000 gallons are not uncommon, but most stills have less than half this capacity. The European practice is to use vertical stills with convex top and concave bottoms.

The top and sides are constructed of half-inch boiler plate, while the bottoms are frequently from 1 to $1\frac{1}{4}$ ins. in thickness and are protected from the direct heat of the fire by a brick arch. The hot gases from the fire are led around the lower half of the still in flues.

The American practice is to use horizontal stills heated on slightly less than half of their cylindrical surface protected by an arch directly over the fire and so designed that the portion of the shell heated may be readily replaced when damaged. The still is equipped with the

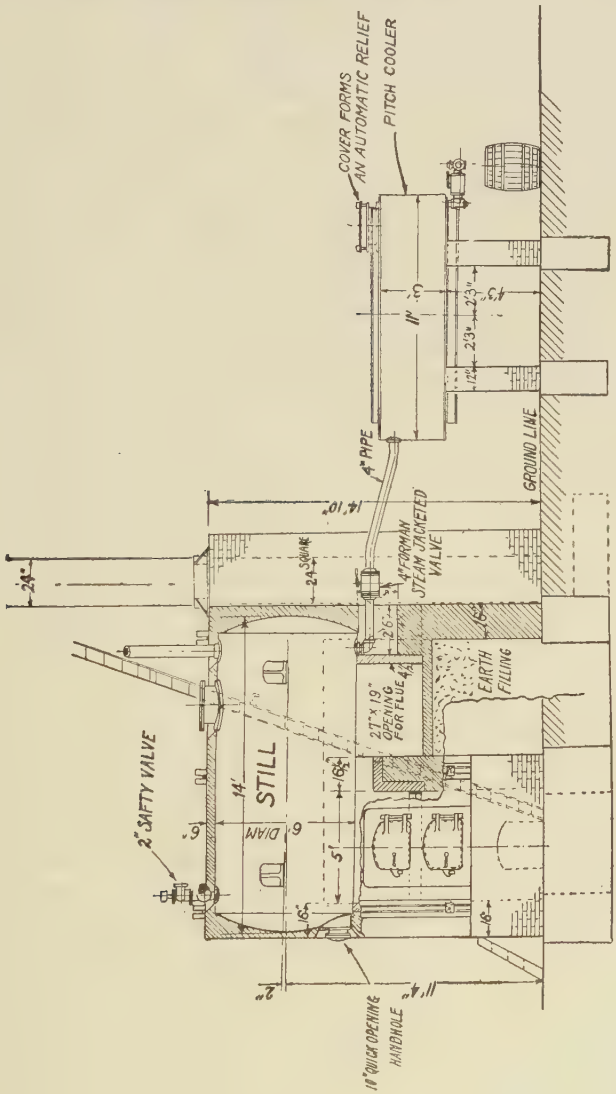


Fig. 240.—American Tar Still.

usual worm, which may be made of either cast- or wrought-iron pipe with receivers, and with a pitch cooler. The objections to cast-iron worms are their numerous joints and greater weight. Since the development of electric welding wrought-iron worms may be made of any desired length with no joints to give trouble. Where high-carbon tars are

worked, stills must be provided with suitable means of agitating to prevent the carbon becoming caked upon the heated part of the shell. Drag chains were formerly employed for this purpose, but compressed air or superheated steam are now more often used, as they serve to keep the still clean and assist in removing the high-boiling oils.

Distillation of Tar. The operation of tar stills varies considerably at different works. The receivers are changed at different temperatures and therefore the products are not uniform. In America it is the more common practice to fraction as light oil until the distillate commences to sink in water, and as heavy oil or creosote oil from that point to pitch. Very little, if any, anthracene is made in this country, as most of the tar is run only to soft pitch with a melting-point between 60 and 80° C.

The European practice is different. From four to six fractions are taken before the pitch and a very large percentage of the tar is run to hard pitch. The following will show the most common fractions and the temperatures of the " cuts."

American Practice		European Practice	
Light oil, or Crude naphtha	Till oil sinks in water about 200° C.	First light oil, or First runnings	To 110° C.
		Light oil, or Second light oil	110° to 200° C.
Heavy oil, Dead oil, or Creosote oil	200° C. to pitch	Carbolic oil	200° to 240° C.
		Creosote oil	240° to 270° C.
		Anthracene oil	270° to pitch
Pitch	Residuum	Pitch	Residuum

In the American refineries during the last few years, there has been more or less tendency to divide the creosote oil fraction into carbolic oil and heavy oil by a cut at about 240° C. in order to recover the tar acids.

The tar is usually charged into the hot still (from the previous run).

The fire is lighted when the charging is about half completed. The fire must be carefully regulated till the rumbling or crackling noise in the still ceases, which denotes that the water has all been driven over. The firing can now be pushed so that the distillate runs at the rate of 200 to 400 gallons per hour. When the desired grade of pitch has been obtained, the fire is drawn and the pitch is run or drawn into the pitch cooler, a closed tank with a manhole having a loose-fitting, free-opening lid which, while it acts as a safety valve, prevents free access of air. The pitch, when sufficiently cooled, is filled directly into barrels for shipment or storage.

The fraction to 200° C. contains water, ammoniacal liquor, crude benzols, pyridine bases, and a part of the naphthalene, heavy oil and phenols. The second fraction from 200° C. to soft pitch (about 270° C.) consists of phenols, naphthalene, heavy oil and some anthracene, though the greater part of the anthracene comes over above 270° C. If the

distillation is continued to hard pitch, a cut could profitably be made at about 270° C., above which point most of the anthracene and anthracene oil would be obtained. The treatment of the fractions as obtained by the American practice only will be considered with incidental allusions to the foreign methods.

The light oil fraction is allowed to settle and the ammoniacal liquor or water is drawn off. The pyridine bases are not as a rule recovered in this country, but are allowed to remain in the heavy oil with the phenols. If it is desired to separate them the light oil is agitated with dilute sulphuric acid in a lead-lined cone-bottomed tank, fitted with a lead-covered propeller, usually supported entirely outside the tank, which mixes the contents. After the pyridine bases have been removed the oil is transferred to a similar iron tank, in which, in order to remove the phenols, it is treated with caustic soda solution of about 1.116 specific gravity. After the carbolates have been drawn off, the oil is charged in a still of 2000 to 3000 gallons capacity, similar to a tar still, but having in addition a column and condenser for fractionally condensing, Figs. 241 and 242, and washing the vapors coming from the still. The following fractions are usually taken:

Crude 90 per cent benzol, to 95° C.
Crude toluol, 95° to 125° C.
Crude solvent naphtha, 125° to 170° C.
Heavy naphtha, 170° to 200° C.
Residue.

The residue consists of naphthalene, heavy oil, and phenols if not previously extracted. It should be added to the second fraction from the tar still.

In some works only three fractions are made in the light-oil still, the first two being combined and this fraction being subjected before washing to another dis-

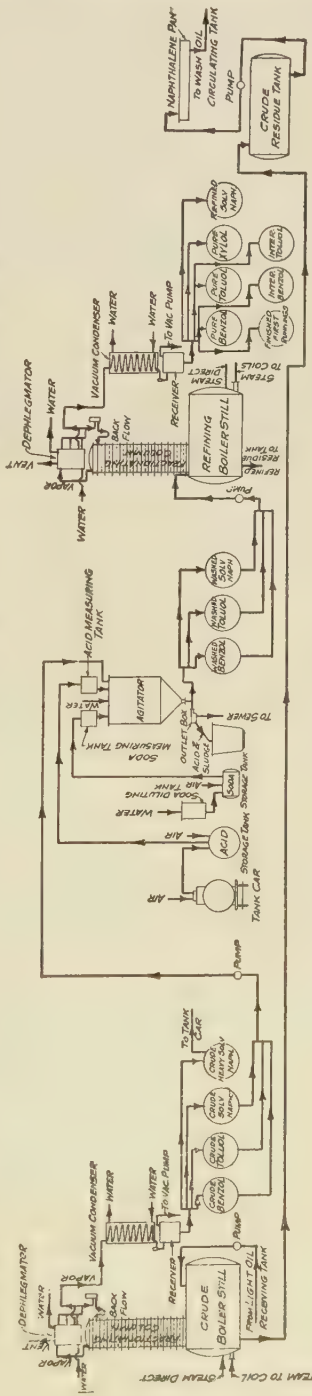


FIG. 241.—Benzol Still.

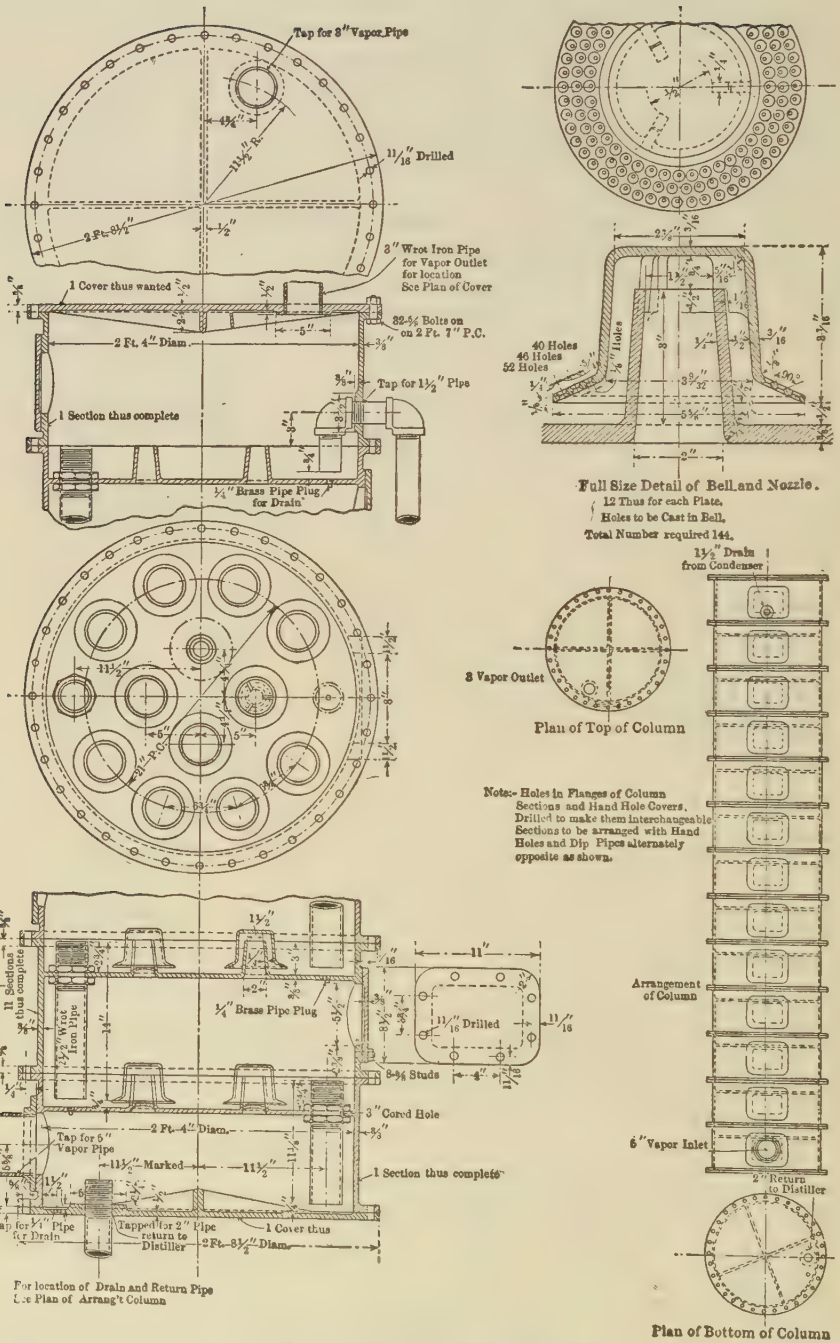

Tap for 3" Vapor Pipe
11/16" Drilled
3" Wrot Iron Pipe for Vapor Outlet for location See Plan of Cover
1 Cover thus wanted
32-⅝ Bolts on on 2 Ft. 7" P.C.
2 Ft. 4" Diam.
Tap for 1½" Pipe
1 Section thus complete
¼" Brass Pipe Plug for Drain
40 Holes
46 Holes
52 Holes
Full Size Detail of Bell and Nozzle.
12 Thus for each Plate.
Holes to be Cast in Bell.
Total Number required 144.
1½" Drain from Condenser
3 Vapor Outlet
Plan of Top of Column
Note:- Holes in Flanges of Column Sections and Hand Hole Covers, Drilled to make them interchangeable Sections to be arranged with Hand Holes and Dip Pipes alternately opposite as shown.
Arrangement of Column
11 Sections thus complete
¼" Brass Pipe Plug
11/16" Drilled
8-⅝ Studs
3" Cored Hole
Tap for 5" Vapor Pipe
1 Section thus complete
Tap for ¼" Pipe for Drain
Tapped for 2" Pipe return to Distiller
1 Cover thus
2 Ft. 8½" Diam.
For location of Drain and Return Pipe See Plan of Arrang't Column
6" Vapor Inlet
2" Return to Distiller
Plan of Bottom of Column

FIG. 242.—Detail of Column.

tillation in a steam-heated column still. The fraction, consisting of benzene, toluene, xylene, and their impurities, would be cut as follows:

Crude 90 per cent benzene	up to 95° C.
Intermediate fraction (which is rerun)	95° to 105° C.
Crude toluene	105° to 120° C.
Crude solvent naphtha added to that fraction	120° to 125° C.

It was early discovered at the Paris Gas Company that the coal gas contained much more aromatic hydrocarbons than the tar.

It was variously estimated at from 15 to 23 times as much but the gas was not seriously considered as a source of benzol while only illuminating gas was manufactured from coal.

When by-product coke ovens became common in Europe, processes were divised to scrub the gas and recover the light oil by continuous distillation, Fig. 243 is a diagram of the usual apparatus employed.

The gas is cooled either by direct contact with water or in tubular coolers to about 70° F. or even less. It is then passed through the series of scrubbers (usually three), where it comes in intimate contact with the cooled wash oil which is about the temperature of the gas entering the system, but should not be more than 2° to 4° F. higher.

The scrubbers may be of almost any design suitable for washing gas, the usual form is shown in Fig. 243, these are tall steel tanks or towers filled with wooden grids to present large surfaces for the contact of the oil and gas.

The wash oil used in the United States is a fluid paraffine oil, specific gravity not more than 0.875 at 18° C., not thickening above 4° C., containing as little olefine as possible, but not more than 10 per cent, giving as little distillate on dry distillation as possible, below 285° C., thermometer in the oil, not more than 1 per cent shall be driven over by steam distillation while collecting a volume of condensed steam equal to the volume of the oil taken for the test, and separating readily from intimate mixtures with water.

The European practice is to use a coal tar heavy oil distilling between 200 and 300° C. at least 90 per cent, and which does not deposit more than 12 per cent naphthalin in all fractions after standing twenty-four hours; Sp. gr. 103 to 105 at $15\frac{1}{2}$° C., or a blast furnace oil which distills at least 85 per cent between 200 and 300° C.

After leaving the first gas scrubber the oil is passed through a heat exchanger, where it is heated by the vapors leaving the still to about 90° C., then through a second heat exchanger, where it is further heated by the debenzolized wash oil, leaving the still to about 110° C.

It is then passed through the preheater and further heated by steam to from 130° to 150° C. After this it passes to the still proper, which is of the continuous type, where the light oil is driven out by steam distillation, leaving the debenzolized oil, which leaves the base of the still,

passes through the oil to oil heat exchanger, the wash oil coolers, and is then ready to be pumped to the scrubbers for a second saturation with light oil from the gas.

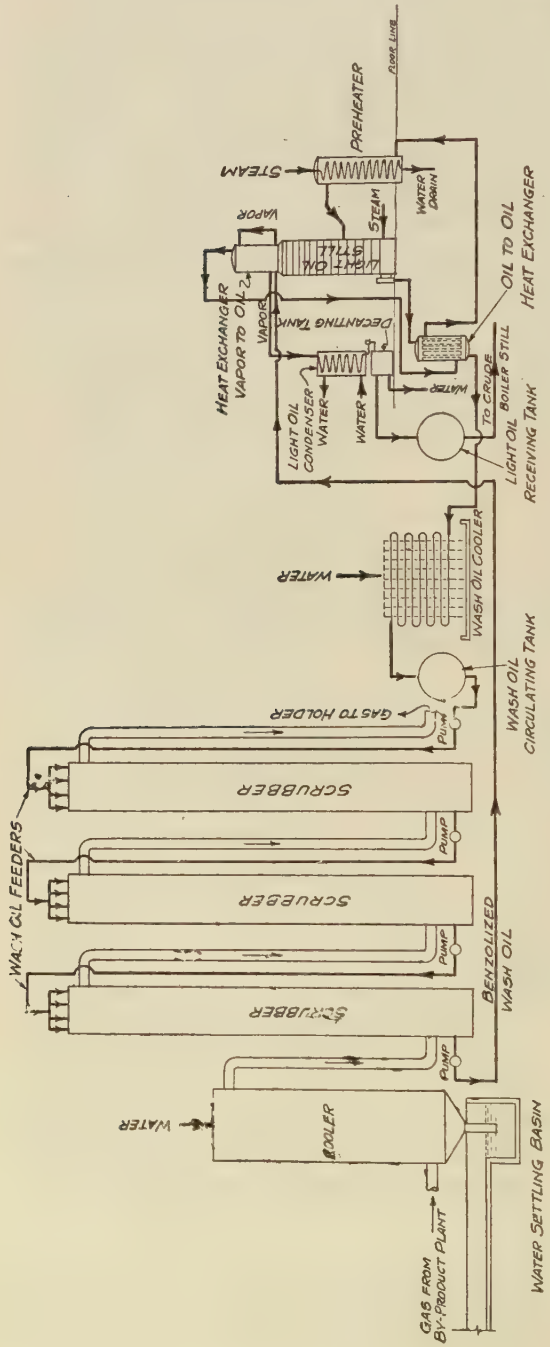


Fig. 243.—Diagram of Apparatus to Recover Light Oil from Gas.

The light oil vapor mixed with steam after passing through the vapor to oil heat exchanger is condensed and flows to the light oil tank after being separated from the condensed steam or water in the decanter. The yield of light oil from coke oven gas is from $2\frac{1}{4}$ to 4 gallons per ton of dry coal carbonized, varying with the volatile content of the coal and much influenced by the type of oven and the heats employed. The relation of the amounts of benzol and toluol produced are also influenced by the heats employed, low heats increasing the production of toluol and xylol.

The control tests necessary to insure proper operation of a plant such as has been described are:

Candlepower and calorific value of gas, both entering and leaving the scrubbers.

Light oil in gas both entering and leaving the scrubbers.

Light oil in wash oil to continuous still.

Light oil in wash oil from the continuous still.

Examination of new wash oil received: Specific gravity, viscosity, emulsification, steam distillation, dry distillation, olefines, thickening at 4° C.

Distillation test of light oil produced with determination of loss and residue above 200° C.

Distillation of frequent samples of distillate to control fractions.

Distillation of samples from storage tanks and residues.

The most common method is to pass a measured volume of gas through a train of bottles containing an absorbent oil. Various oils are used: paraffin oil, wash oil, oleic acid and cottonseed oil are among those proposed.

A modified Lessing scrubber has come into favor of late as the standard apparatus to test for scrubber efficiency.

This light oil is usually fractioned in a steam-heated column still so as to yield crude benzol distilling 90 per cent to 100 °C., crude toluol distilling about 5 per cent to 100° C. and 90 per cent to 120° C., crude solvent naphtha distilling about 5 per cent to 130° C. and 90 per cent to 160° C., crude heavy solvent naphtha distilling about 5 per cent to 160° C. and 90 per cent to 200° C. The residue consists of wash oil and crude naphthalene. It is transferred to pans and allowed to become cold when the naphthalene crystallizes. The wash oil is drained off and returned to the wash oil circulating tank to be used over again.

The crude fractions are washed and refined in the same manner as similar fractions of the light oil from tar. The recovery of light oil from coke oven gas has become general in American by-product coke oven practice during the past two years though it has been employed by one company operating several coke oven plants for several years.

The purification of these fractions consists in the polymerization of the unsaturated compounds and the removal of the dissolved polymerized hydrocarbons by distillation. The oil is treated with successive small portions of sulphuric acid, 1.835 sp.gr., in an agitator tank, Fig. 244, similar to the one used for pyridine extraction. The agitator for washing with strong acid can be lined with lead. A better construction is of cast iron with leaded joints of the bell-and-spigot type, similar to those used on cast-iron water pipe, and with a conical bottom to permit of complete separation of the acid and the oil. The several small portions of acid are agitated with the oil, allowed to settle for a few minutes and the acid tar composed of spent acid and polymerized hydrocarbons drawn off. Care must be taken to remove the acid tar completely after the final application of acid. The acid necessary for a satisfactory purification of the oil should be determined by a laboratory test after each addition of acid. If too little acid is used the tarry products are apt to separate and clog the draw-off, and if too much is used the spent acid will be very thin and fluid. A good wash is usually obtained when

between $\frac{1}{3}$ and $\frac{3}{4}$ of a pound of acid is used per U. S. gallon. This is applied in four to six successive portions. In this way a better wash and a larger yield will result together with a saving of acid. Formerly it was usual to wash the oil two or three times with water, but as this serves only to reduce slightly the caustic soda necessary to remove all the acid remaining in the oil, and as it adds materially to the time required to complete the wash, it has been in most cases discontinued. The oil is finally treated with sufficient 10 per cent caustic soda solution to remove all traces of the acid. The washed oil is sometimes distilled in a steam-heated simple still, but this is not necessary with the fractions of light oil recovered from coal gas, which leaves behind, as a viscid mass, the polymerization products that were dissolved in the oil. This residue is reported to have some application in waterproofing paper.

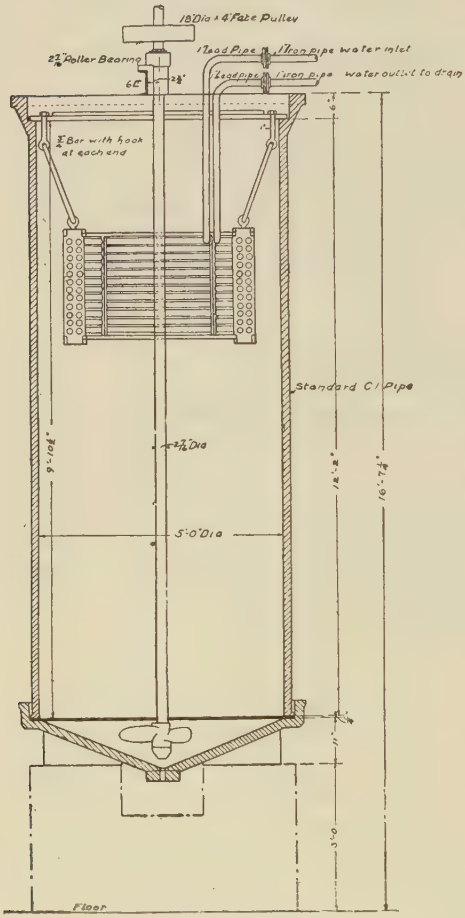


FIG. 244.—Benzol Agitator.

The final fractioning of the refined oils is conducted in steam-heated stills with columns similar to those used for the rectification of spirits. They consist, Fig. 241, of a series of plates, inclosed in a shell, with nozzles extending from their upper side, over which are inverted saucers or caps so designed as thoroughly to mingle the ascending vapors with the descending condensed oils and yet prevent foaming as far as possible.

These columns were formerly made entirely of copper, as is the practice in alcohol rectification, but cast iron, wrought iron and steel are better materials, cost less and are not acted upon by the sulphur compounds contained in the oils. Columns frequently have as many as thirty sections to do the best work, though by far the greater part of the fractioning is done in the first ten or twelve sections.

Benzol. The crude benzols from light oil are colorless when freshly distilled, but they soon become a pale straw color and continue to

darken for some time. They are known in the trade as crude or "straw-color" benzols of the various grades.

Fraction.	Specific Gravity.	5–10%	90%	Dry.	Flash-point.
Straw-color benzol..... Crude 90 per cent benzol .	0.860–0.885	80° C.	100° C.	120° C.	below 0° C.
Straw-color toluol..... Crude toluol.....	0.860–0.875	100° C.	120° C.	140° C.	below 0° C.
Crude solvent naphtha.....	0.870–0.885	130° C.	160° C.	190° C.	22–26° C.
Heavy naphtha.....	0.925–0.940	160° C.	210° C.	220° C.	43–45° C.

These crude oils are chiefly used as solvents where their odors are not objectionable. Crude solvent naphtha and heavy naphtha are also used as thinners in certain cheap paints.

Of the refined oils three are separated in a pure state, C.P. benzol, C.P. toluol, and xylol. The first two distill entirely within 2° C., while the last is a mixture of the three xylenes and distills from 135 to 145° C.

C.P. benzol or benzene, has sp.gr. .875 to .884. Freezing-point 4° C., boiling-point 80.2° C. It should distill completely within 2° C., be colorless and have the characteristic odor. It should not be colored on shaking with one-third its volume of C P. sulphuric acid, 1.84 sp.gr. (967 H_2SO_4), and the acid should be only slightly colored after standing for one-quarter of an hour. It should be free from thiophens, contain only traces of carbon disulphide and from 1 to 3 per cent of inert paraffines.

Toluol. C.P. toluol or toluene has sp.gr. .865 to .876, boiling-point 111° C. It should be colorless and have the characteristic aromatic odor. It should not be colored by shaking with one-third its volume of C.P. sulphuric acid, sp.gr. 1.84, and the acid layer should not be colored deeper than a pale straw after standing for one-quarter hour. In other respects it should answer the specifications for C.P. benzol.

The following refined commercial fractions are colorless and should not be colored by shaking with one-half their volume of C.P. sulphuric acid, nor should the acid layer become colored deeper than a straw color in one-half an hour except in the case of 160° and 200° naphthas, when the acid may become colored deep red.

Fractions.	Specific Gravity.	Temperatures Noted in Distillation.			Flash-point.
		80° C.–90° C.	100° C.	120° C.	
100% benzol.....	0.875–0.885	5–10%–90–95%	dry		below 0° C.
90% benzol.....	0.865–0.880	0%	90–92%	dry	below 0° C.
		100° C.	120° C.	135° C.	
50% benzol.....	0.862–0.880	50–52%	90–92%	dry	below 0° C.
Commercial toluol	0.865–0.875	0–5%	90–95%	dry	below 0° C.
		130° C.	160° C.	185° C.	
Solvent or 160° naphtha.....	0.860–0.870	0.5%	90–92%	dry	22–26° C.
		160° C.	200° C.	215° C.	
200° naphtha....	0.879–0.882	0–10%	90–92%	dry	42–45° C.

German number	English name	85°	90°	95°	100°	105°	110°	115°	120°	125°	130°	135°	140°	150°	160°	170°	180°	190°
I	90% benzol	48	78	87.5	91.5				dry									
II	50% benzol		3		52	67	77	84	90									
III	Commercial toluol			31		11	49	79	91	95								
IV	Carburetting naphtha										30	60	87					
V	Solvent naphtha												20	75	91			
VI	No. 2 solvent naphtha													5	50	84		
Heavy benzol	200° naphtha															45	82	91
Technisches benzol	100% benzol		90		dry													

The last two are not so well washed, therefore the acid becomes more deeply colored.

In Germany the refined "benzols" are now known as numbers which are compared below to our grades. The distillation of the German grades are also shown.

Creosote or Heavy Oil. The fraction from the tar still between 200 and 270° C., and sometimes even higher, contains most of the phenols, naphthalene, anthracene, and the accompanying oils. Anthracene will be found in large quantities only when the distillation of the tar is carried to hard pitch.

If it is desired to remove the tar acids (phenols) the oil is agitated at a temperature of 50 to 70° C. with sufficient caustic soda solution sp.gr. 1.116, to combine with them. The alkaline liquor is allowed to settle and is drawn off, after which the oil is run into shallow tanks or pans, where a large part of the naphthalene separates out as a mass of crystals when the oil cools. It is possible to treat the oil with successive portions of the caustic soda solution so as to obtain, first an alkaline solution in which sodium phenolate preponderates; second an equally pure sodium cresylate; and third an unsaturated solution of caustic soda and sodium cresylate which is used as the first portion on the succeeding charge.

The portion containing principally sodium phenolate is boiled by direct steam, and air is passed through the boiling liquid to remove naphthalene, hydrocarbon oils, and pyridine bases. In some works the distillate from the boiling carbolate is collected and worked for pyridine and naphtha, in which case the boiling is done by fire-heated still instead of by direct steam. The distillate is collected until the purification is nearly complete, when the manhole is opened and direct steam and air blown through the liquor. After this treatment the carbolate of soda should be soluble in water without turbidity. The purified phenolate solution is allowed to become cold and is saturated with carbonic acid gas, usually obtained from the flue gases from the steam boilers. Finally, after the carbonate of soda solution formed has been drawn off, the decomposition is completed, in a lead-lined tank, by a little dilute sulphuric acid, which also aids the separation of the phenol from the aqueous solution. The sodium sulphate solution is carefully and completely drawn off. The crude phenol thus obtained contains from 20 to 25 per cent water and tar. These are removed by distillation in a still similar to a tar still, although much smaller. The dry, crude phenol is fractioned in column stills heated by direct fire or superheated steam, but otherwise the stills are similar to those used for benzols. These yield, first, a crystallizable phenol, second, a fraction not sufficiently rich in phenol to crystallize, and a third fraction containing principally cresols. The fractioning of the crude phenols is conducted at reduced pressure at some works. By this process, owing to the low temperature of the distillation, a larger yield of phenol is obtained.

The crystallizable fraction is further purified by repeated crystallization with the aid of refrigeration and with the addition in the last crystallization of water to dilute the cresols present. Finally, these purified crystals are redistilled, condensed in block-tin worms and collected in tin receivers so arranged that they can be heated to melt the phenol in order that it may run in a liquid state into containers.

A properly purified phenol will remain white for more than a year, showing no trace of the red color commonly seen in crystal carbolic acid.

The second portion of the alkaline liquor from the treatment of the dead oil, containing largely cresylate of soda, is saturated with carbonic and sulphuric acids in the same manner as is the portion rich in phenol. It is not customary to boil the cresylate of soda to remove the oils and pyridine bases unless it is desired to make pure cresol. The crude cresol is freed from tar and water by distillation and is then marketable as 95 to 100 per cent cresylic acid.

Phenol, carbolic acid, hydroxy-benzene, C_6H_5OH, when pure, is a white, crystalline mass, with sp.gr. 1.084 at 0° C., melting at 42° C., boiling at 182° C., having a characteristic odor and when very dilute a sweetish taste.

It is soluble in all proportions in alcohol, ether, chloroform, glacial acetic acid, and glycerine. It liquefies on the addition of 14 to 15 per cent of water, and thus becomes the No. 4 carbolic acid of commerce. It dissolves in about 20 parts of water at 25° C. It is a corrosive and irritant poison. Undiluted alcohol is one of the best washes for phenol burns. Carbolic acid is largely used in medicine and surgery as an antiseptic and disinfectant and in the arts in the manufacture of dyes. It is employed in the manufacture of picric acid, trinitrophenol, which finds a large use in the manufacture of high explosives, and is also used as a yellow dye.

Cresol, cresylic acid, hydroxytoluene, $C_6H_4CH_3OH$, is a mixture of three isomers, has a sp.gr. of 1.032 to 1.038 at 25° C., and distills between 190° and 205° C. It is used as an antiseptic and disinfectant and is much less corrosive than phenol and is a more efficient antiseptic.[1]

The three isomers composing cresol have the following properties:

Orthocresol, orthocresylic acid, ortho-oxy-toluene, orthomethylphenol, $C_6H_2OH(CH_3)$, with the CH_3 and OH groups in the (1–2) position, is a white crystalline substance melting at 28 to 30° C., into a colorless liquid and boiling at 187 to 189° C. It is soluble in thirty parts of water, in alcohol, ether, chloroform, and the caustic alkalies.

Metacresol, metacresylic acid, meta-oxy-toluene, metamethylphenol, has the CH_3 and OH groups placed in the (1–3) position, and is a colorless liquid, sp.gr. 1.0498 to 1.05 at 0° C. It boils at 202°, is

[1] Dr. A. P. Hitchins has informed me in a private communication that the toxicity of phenols and cresols are directly proportional to their germicidal value and that cresylic acid is about three times as efficient a bactericide as phenol.

soluble in alcohol, ether, chloroform, caustic alkalies, and slightly in water.

Paracresol, paracresylic acid, para-oxy-toluene, paramethylphenol, with the CH_3 and OH groups placed in the (1–4) position, is a white crystalline mass, melting at 36° C., and boiling at 198° C. It is soluble in alcohol, ether, chloroform, caustic alkalies, and slightly in water.

Xylenol, di-methyl-phenol, hydroxy-xylene. The six possible isomers are probably present in the fraction of crude cresylic acid boiling between 210° and 230° C. and which has a sp.gr. between 1.02 and 1.03 at 15° C. They are on the whole considerably more soluble in water and less corrosive than the cresols. They are principally used in disinfectants of the "creolin" type on account of their high phenol coefficient which is between ten and twelve. They are not generally separated from the crysilic acid except when pure cresols are made.

Naphthalene. The heavy oil fraction, if the removal of the naphthalene is desired, is run into shallow tanks or pans, either from the still or after the tar acids have been extracted, and allowed to become cold, when the larger part of the naphthalene crystallizes. The oil is drawn off and the crystals are either shoveled into piles to drain or are passed through a centrifugal which leaves the crystals nearly dry and in condition for market as "drained creosote salts" or crude naphthalene.

Refining naphthalene consists in freeing it from adhering heavy oil and from unsaturated, easily oxidized compounds. The crude material should be in a coarse crystalline condition to allow of the proper extraction of the oil. If it is in a slimy state it should be recrystallized. The crystals are either washed with hot water in centrifugals, which removes the larger part of the adhering oil, or they are hot pressed in hydraulic presses. The latter process is more expensive and less efficient than the former. After this operation the naphthalene should have a melting-point of not less than 76° C., and will still contain from 4 to 6 per cent of oils. The partly purified naphthalene is now distilled, to remove the tarry bodies that have been carried forward from the original tar. This process is conducted in plain, externally fired iron stills, similar to tar stills, but with lead worms. The distillate is kept in a melted state and run into lead-lined agitators similar to those used for benzols, and washed with sulphuric acid, 1.835 sp.gr., several waters, and finally with caustic soda solution, of about 1.116 sp.gr. Great care must be taken to remove as much as possible of the acid before the first water is added, so as to prevent the tarry polymerization products from being redissolved by the naphthalene. The soda solution is drawn off completely, as small amounts of soda will cause the bottom of the still to be rapidly burned out. It is necessary to reject the first portion "heads," and the last portion, "tails," of the distillate from the final distillation of refined naphthalene, as the "heads" are discolored by the washings of the worm and with water containing dissolved bases, metallic

salts, etc., while the oils are concentrated in the "tails." The sum of the rejected portions should not exceed ½ to 1 per cent of the distillate.

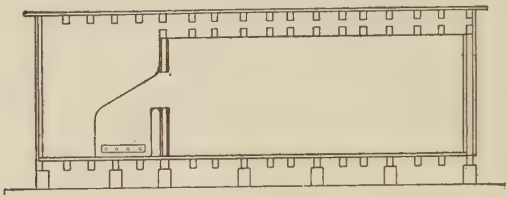


Fig. 245.—Naphthalene Subliming Plant.

The water-white refined naphthalene is run into shallow pans to cool, when it can be broken up and sold as lump, or is run into copper tanks heated by steam, from which it is available for casting into balls, etc., or for use in the subliming pans. Subliming pans, Fig. 245, are large shallow iron tanks heated by steam and connected by an iron hood with a smoothly sheathed room in which the sublimed vapors condense in transparent plates, "flake naphthalene." About 150° C. seems to be the most satisfactory temperature in the subliming pans. A higher temperature can be economically employed in winter and a somewhat lower one in summer. Naphthalene, $C_{10}H_8$, is a solid hydrocarbon at ordinary temperatures, melting at 79–80° C., and boiling at 218° C. Its specific gravity in the solid state is 1.151 at 15° C. and in the liquid state it is 0.9778 at 80° C. It volatilizes at ordinary temperatures and very readily on the steam bath. It crystallizes in transparent rhombic plates, which are slightly soluble in hot water but insoluble in cold water. It is very soluble in chloroform, benzene, ether, alcohol, methyl alcohol and paraffine.

The purity of refined naphthalene is indicated by the faint purple or pink tint when a lump is dissolved in hot concentrated sulphuric acid. If the acid is turned a deep red the sample is likely to become discolored on standing. Naphthalene is used as the starting-point of several classes of colors, including nearly all of the azo-colors and for artificial indigo, in candles, celluloid, as a substitute for camphor to prevent moths in woolens, and to some small extent as a gas enricher in lights of the albo-carbon type. It readily nitrates directly to mononitro naphthalene, which crystallizes in yellow needles, with sp.gr. 1.331 at 4° C., melting at 56° C., and boiling at 304° C. It is easily soluble in alcohol and petroleum oils. Its principal uses are the manufacture of certain smokeless powders and to remove the fluorescence from petroleum oils, for which latter purpose from 2 to 3 per cent is used.

Anthracene. This oil is the portion of the distillate from coal tar which vaporizes above 270° C. At this temperature a cut should be made if the distillation is carried to hard pitch. This oil boils between 250 and 400° C, and has a specific gravity of nearly 1.1. Its color is yellowish-green when first made, but it darkens to almost black. It

contains besides anthracene, naphthalene, methylnaphthalene, pyrene, acridene, phenanthracene, fluorene, etc., all of which are solids, except methylnaphthalene, and a mixture of oil of which we know very little.

The anthracene fraction is run into shallow tanks and the solid compounds separate out on cooling. This process requires from one to two weeks.

Refrigeration has been tried to shorten the time, but it makes the oils more viscid and the separated crude anthracene much more impure. The semi-solid mass is transferred to bag filters or to a filter press and as much as possible of the oil driven out by compressed air. The nearly dry cakes from the bags or filter press, containing about 10 to 15 per cent anthracene, are subjected to a pressure of from 50,000 to 70,000 lbs. in hydraulic presses so arranged that they may be kept hot by steam coils or steam-heated plates. This treatment brings the anthracene content to from 25 to 35 per cent. These press-cakes are ground and purified by washing in a closed agitator with hot solvent naphtha from the light oil.

Lower boiling benzols have been used for this purpose, but they dissolve the anthracene itself. The whole charge, when thoroughly mixed, which may require several hours, is run into a closed filter and the solvent removed by compressed air. Pyridine bases are said to be a better solvent for the anthracene impurities than solvent naphtha and is said to yield 80 per cent anthracene, while 70 to 75 per cent is the limit with solvent naphtha.

A somewhat more pure anthracene is produced by the sublimation of the washed material. The subliming pans are similar to those used for naphthalene except that they are heated by fire and have jets of superheated steam impinging upon the surface of the melted anthracene. The vapors are condensed by water jets. The oil from the first crystallization of the crude anthracene is distilled in a clean still till crystals appear upon cooling the distillate, when the residue containing the anthracene is run into pans and treated the same as the original fraction.

When the oil will yield no more anthracene it is used to soften, "cut back," pitch, as "Carbolineum Avenarius," for the treatment of timber, and mixed with the creosote oil.

Anthracene, $C_{14}H_{10}$, was discovered by Dumas and Laurent in 1832 and recognized as a characteristic constituent of coal tar by Fritzsche in 1867. It boils at 363° C., melts at 213° C., and has a specific gravity of 1.147 at 15° C. It crystallizes, when pure, in white or yellow rhombic plates with a blue fluorescence. It is soluble in benzene, ether, chloroform, carbon bisulphide, and in hot alcohol, but only sparingly soluble in cold alcohol.

It is slowly converted by sunlight into paranthracene. It is of great importance commercially as the starting-point for the synthetical alizarines.

Valuation of Tar and Tar Products. Sampling is of the utmost importance with the tars and the crude oils. They frequently contain two or more substances that have more or less tendency to separate on standing, such as water and ammoniacal liquor, and which are difficult to reincorporate evenly. Where possible drip samples should be taken as the materials are being pumped.

Small drip openings are so prone to become clogged with particles of dirt or fine crystals that it is always well to make the original drip sample as large as possible. A tank of 100 gallons' capacity can easily be arranged to catch the drip. This can be thoroughly mixed and reduced samples accurately drawn by a large pipette called a "thief."

FIG. 246.

The drip sampling should begin as soon as the pump is working freely and should continue without diminution to the end. With oils that have solidified care should be observed that they are completely remelted and well mixed before drawing a sample. Where it is impossible to take a drip sample a "thief" may be used. A satisfactory "thief" for small tanks or tank cars can be made from a one-inch iron pipe with a round water-way cock, operated by chains, at the lower end. In large tanks and when a proper "thief" is not available, a bottle will serve to obtain a fairly good sample. The bottle is weighted, corked, sunk to the bottom of the tank, when the cork is pulled by a string previously attached and the bottle evenly and rapidly drawn from the tank. If the bottle is not completely full the sample is considered a representative one. The final samples of tar, light oil, and heavy oil should be not less than one gallon, while a pint usually suffices for naphthas, benzols, etc.

The Examination of Tar. While, as suggested by Allen, Lunge, and others, more definite information can be obtained the larger the scale of operation, yet it has become quite established to work with a gallon sample. The tar sample should be poured into a dish or bucket and mixed by vigorous stirring, to redistribute evenly through the sample any water that may have separated.

The complete examination of tar consists of the following:

Determination of the water by distillation;

Distillation of the tar;

Specific gravity of the dry tar;

Free carbon of dry tar.

Examination of the light oil, heavy oil, and pitch.

The still now largely used in this country for tar distillations and water determinations, Fig. 247, in tar was described by H. W. Jayne (J. A. C. S., XXV., p. 81).

It is made of copper $3\frac{1}{2}$ ins. in diameter, with straight sides 6 ins. high, a heavy turned brass ring at the top, a brass lid, held in place by

a single clamp over the top. The lid has two holes, one for a $\frac{1}{4}$-in. pipe plug and the other fitted with a short piece of $\frac{3}{4}$-in. brass pipe tapered on the inside to fit the cork which carries the distilling tube or adapter. This still can be easily cleaned, which is an important provision in a tar still. A paper gasket was used, but the small valve packings similar to vulcabeston are equally satisfactory and may be used repeatedly. The condenser consists of a copper trough through which passes a glass tube about $\frac{1}{2}$ in. internal diameter and 24 ins. long. This form of condenser is ordinarily used without running water. It allows of heating the water when the naphthalene fraction begins to solidify in the tube and drawing it off altogether when the still higher fractions would be liable to crack the glass. It is very efficient for volatile liquids, as the tube can be easily packed with ice or with a freezing mixture. The cut shows the still and condenser mounted for use. A larger still $4\frac{1}{2}$ ins. in diameter and 8 ins. high of the same design should be used if 1000 c.c. of tar are distilled or dried.

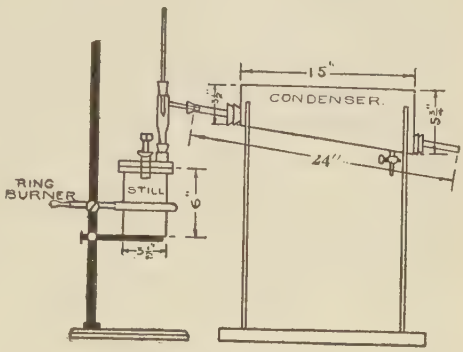


FIG. 247.

The Estimation of Water. Of the well-mixed sample 200 to 600 c.c. is diluted with about 100 c.c. of high-boiling water-free oil, to prevent boiling over, crude solvent or heavy naphtha, is usually distilled in the smaller still above described. The heat is at first applied by a ring burner designed to throw the flame toward the still and adjusted so that the flame strikes the still at or above the level of the tar. When the temperature has reached about 150° C., an ordinary Bunsen burner is lighted under the bottom of the still. The distillation is carried to from 200 to 205° C., to be sure that none of the water is held back by the tar or by the apparatus. The distillate is collected in a graduated cylinder and is usually reported as per cent by volume, but if desired may be converted into per cent by weight. The thinning with dry oil may be omitted in many cases and the specific gravity and free carbon can be determined on the dry tar thus obtained after carefully reincorporating the oil carried over by the water.

Specific Gravity. It is obviously quite troublesome, if not impossible, to thoroughly clean the ordinary specific gravity bottle of tar, and there is more tendency for small air bubbles to cling to the sides than in a bottle with vertical sides. For the determination of the specific gravity of tars Lunge has suggested a tall weighing bottle about 1 in.

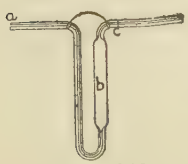


FIG. 248.

in diameter and 3 ins. high, with a glass stopper having a small vent "v" ground in the joint. (Fig. 248.)

The process is the same as for the specific gravity of solids. First fill the tared bottle nearly full of tar, then the balance with water, and finally completely with water. The weighed bottle (*a*) is two-thirds filled with tar and set in hot water or on a steam bath till the air bubbles have all disappeared. It is then cooled to 15° C. and weighed (*b*). Water is added to fill the bottle, the stopper forcing out the surplus through the vent; it is carefully dried and the weight taken (*c*). The bottle is now filled with water at 15° C. and weighed again (*d*).

$$\text{Sp.gr.} = \frac{b-a}{d+b-(a+c)}.$$

The water and specific gravity of the dry tar are usually a satisfactory index of the quality of the tar. Kohler (Z. angew. Chem., 1888, p. 677) has shown that the specific gravity of dry tar reflects the per cent of free carbon. This complex mixture of organic compounds containing, according to Donath and Asriel, (Chem. Centr., 1903, I., p. 1099), carbon 89.2 per cent, hydrogen 2.3 per cent, nitrogen 0.7 per cent, oxygen 7.13 per cent, ash 0.67 per cent, is quite similar to anthracite coal except for the ash and moisture. It is usual to ascribe a part of this to coal dust carried over from the retorts, but the low ash would seem to preclude more than 8 per cent of coal dust in it.

Free Carbon. Free carbon is, however, one of the most important factors in determining the value of a tar for its more important uses. Many schemes have been proposed for its isolation, based upon different solvents, carbon bisulphide, aniline, glacial acetic acid, and members of the benzene series.

Its determination is always made on the dry tar, and the benzenes are the solvents mostly used in America. The determination is carried out as follows:

One to five grams of tar are weighed in a small beaker, hot toluene added, well mixed and allowed to settle. Two tared S. & S. fat extraction thimbles, the inner one 22×80 mm. and the outer one large enough for a loose fit, are suspended over a beaker or an Erlenmeyer flask, saturated with hot toluene, and the supernatant toluene decanted from the tar through the thimbles. The tar is washed by decantation several times with hot toluene, then three times with hot C.P. benzene, finally the residue is washed into the inner thimble. The thimbles are transferred to a Soxhlet extractor and extracted with benzene. If the benzene becomes too contaminated with tarry extract it is discarded and a fresh portion used to continue the process. When the benzene no longer becomes colored the extraction is complete, the thimbles are dried in a steam bath and finally at 110° C., and weighed.

Volatile Portions. The study of the distillation products of tar is

made by distilling 1000 c.c. of the well-mixed sample in a copper still similar in design to those used for the water determination, but with a capacity of 2000 c.c. This distillation is carried by careful heating with a ring burner to 200° C. The distillate is received in a graduated separatory funnel and the percentage of water is noted. The oil is separated and returned to the still as soon as the contents has become cooled to room temperature.

The distillation is started anew and carried to 205° C., when the receiver is changed. The distillation is continued till the residue has a melting-point of 60° C. This is a somewhat troublesome operation, but it is greatly facilitated by collecting the distillate from each 10° C. increase in temperature in separate receivers, usually small graduated cylinders. Thus to cut the residue back to 60° C., if a too high melting-point is obtained, successive fractions may be poured back. When the correct melting-point, 60° C., is reached, the temperature is noted and the pitch is poured into a shallow pan.

The light oil fraction is mixed and its specific gravity taken at 15.5° or 3° C. above the limpid point. A correction of .0008 is added to the specific gravity for each degree above 15.5° C. The tar acids, the phenols, are extracted from the whole fraction if less than 100 c.c. by shaking with one-half its volume of 10 per cent caustic soda solution in a graduated separatory funnel. After carefully separating the soda solution the loss is noted. The treatment with caustic soda is repeated till the loss becomes constant. This loss equals the tar acids and is usually reported as per cent by volume. The carbolic acid in the soda solution can be set free by dilute sulphuric acid and the volume noted, as a check, 20 per cent being deducted for included water.

The oil free from tar acids is fractioned by a Lebel-Henninger tube to 170° C., 170 to 200° C., and a residue. The fraction to 170° C. is considered crude benzols, including benzene, toluene, xylene, and solvent naphtha. The second fraction, 170 200° C., is heavy naphtha and the residue is heavy oil. The residue is cooled to 0° C. for 15 minutes and drained on a tared filter paper, by suction, pressed, and weighed. This is the naphthalene often spoken of as pressed naphthalene. The specific gravity and distillation of each fraction, as well as of the residue, should be recorded. As these fractions are often quite small, a 1-c.c. Sprengel specific gravity tube, modified as shown in Fig. 191, with *a* and *c* of capillary tubing, which require no caps, even when the specific gravities of oils as volatile as benzene are taken, has been found accurate and rapid.

The fraction from 200° C. to soft pitch from the original tar is the creosote oil, the specific gravity of which is taken at 15.5° C., or if not limpid at that temperature, 3° above the limpid point, using the same correction factor as for the specific gravity of light oil. A portion of 100 c.c. is distilled in a 200-c.c. distilling flask, noting the distillate

at each even 10° C., also at 205 and 315° C. Of this, 90 per cent should be distilled off and the tar acids determined as described for the light oil fraction, the whole 90 c.c. being extracted. The extracted oil is cooled to 0° C. for fifteen minutes and the naphthalene drained, pressed, and weighed as explained above. The per cent of naphthalene is calculated to the weight of the original 100 c.c. of heavy oil.

The Creosoter's test, handed down from English practice, having been specified by Sir Fredk. Abel in the early eighties, with the latest modifications is as follows: Of the melted oil, 100 gms. is weighed into a tared tubulated, 8-oz. retort. A nitrogen-filled thermometer graduated in degrees to 350° C. is fixed in the tubulature with the bottom of the bulb one-half an inch above the surface of the oil. The retort is set on two thicknesses of a 20-mesh wire gauze at least 6 ins. square and the whole bulb and at least 2 ins. of the neck covered with a shield of $\frac{1}{8}$-in. thick asbestos board to prevent radiation of the heat. The horizontal distance from the bulb of the thermometer to the end of the condenser tube must not be less than 21 ins., nor more than 24 ins. The fractions are collected in tared bottles or cylinders and weighed. The per cent by weight of the following fractions are reported:

Up to 170° C., water and light oils;
170 to 200° C., } light oils and phenols;
200 to 205° C., }
205 to 210° C., } naphthalene, naphthalene oil, and phenols;
210 to 235° C., }
235 to 270° C., naphthalene and anthracene oil;
270 to 315° C., anthracene and anthracene oil;
315° C., up, residue in the retort.

For all practical purposes it is sufficient to report the fractions as follows:

Below 200° C., water, light oil, and some phenols;
200 to 210° C., light oil and phenols with some naphthalene;
210 to 235° C., naphthalene, naphthalene oil, and phenols;
235 to 315° C., anthracene, anthracene oil, and some naphthalene;
Above 315° C., residue.

The distillation should be conducted so that it is completed in from thirty-five to forty-five minutes and the fraction 210 to 235° C. is collected in from ten to twelve minutes. The distillation should be made on the dry oil if more than allowed amount of water is present, which varies from 2 to 5 per cent in different specifications. If it is necessary to dry the oil it is done by heating to 205° C. in a retort with a condenser attached. The oil in the distillate is separated from the water and again mixed with that in the retort.

The specific gravity is determined with a hydrometer at a few degrees above the limpid point and the factor .0008 used to correct to 15.5° C.

The U. S. Forestry Service prescribes that the distillation should be made in a special Hempel distilling flask. 250 gms. of the oil are weighed into the tared flask; a loose plug of coarse platinum wire in the constricted portion of the neck supports the 200 large glass beads which partly fill the column. The flask is supported on an asbestos board in which a hole with a notched outline is cut almost as large as the largest diameter of the bulb of the flask. The portion of the bulb above the asbestos board and below the column is covered by an asbestos board box, and an Erlenmeyer-Argand burner is used as the source of heat.

The distillation is run at the rate of one drop per second and the following fractions collected:

Up to 170° C.,	245 to 255° C.,
170 to 205° C.,	255 to 285° C.,
205 to 225° C.,	285 to 295° C.,
225 to 235° C.,	295 to 305° C.,
235 to 245° C.,	305 to 320° C.

The indices of refraction of the different fractions between 235 and 305° C. are determined at 60° C. in a refractometer with light compensator. The fraction distilling between 305 and 320° C. is treated with four or five times its volume of concentrated sulphuric acid and placed in the steam bath for at least one hour with frequent shaking. It is then transferred to a convenient measuring apparatus graduated in tenths of a cubic centimeter. The flask is rinsed twice with concentrated sulphuric acid and the rinsings added to the main portion. After standing for one hour the unsulphonated oil, if any, is read and the ratio of its volume in cubic centimeters to the weight in grams of the original oil is calculated. The index of refraction of this residue should be low (1.49 to 1.50) and it should not be soluble in 10 per cent caustic soda solution.

The Forest Service have specifications for several grades of creosote oil based on the above analysis. Grade 1 should be derived from the distillation of pure coal tar and free from any adulteration whatever or any undistilled tar.

For water in excess of 3 per cent deduction will be made. It shall have a specific gravity at 60° C. of not less than 1.04. When analyzed by the above method it shall have the following fractions calculated on the moisture-free basis when more than 3 per cent of water is present.

Up to 205° C., not more than 5 per cent.;
Up to 235° C., not more than 40 nor less than 5 per cent;
Up to 250° C., not more than 50 nor less than 15 per cent;
Up to 295° C., not more than 65 nor less than 30 per cent;
At 355° C., the residue must be soft and not sticky.

The sulphonation test of the fraction between 305 and 320° C. shall leave no oily residue insoluble in caustic soda solution.

The indices of refraction at 60° C., shall be as follows for the following fractions:

At 250° C., not less than 1.593, nor more than 1.602;
At 290° C., not less than 1.615, nor more than 1.622;
At 300° C., not less than 1.625, nor more than 1.632.

Grade 2 should be derived from the distillation of coal or water gas tar, or from a mixture of these two. It must not contain any undistilled tar.

If it contains more than 5 per cent of water a reduction in price will be made corresponding to the excess. The specific gravity at 60° C. shall not be less than 1.03. When analyzed by the Forest Service method, it shall have the following fractions calculated on the moisture-free basis:

Up to 205° C., not more than 20 per cent,
Up to 235° C., not more than 55, nor less than 5 per cent;
Up to 250° C., not more than 65, nor less than 15 per cent;
Up to 295° C., not more than 80, nor less than 30 per cent.

The indices of refraction at 60° C. shall be as follows:

At 250° C., not less than 1.59;
At 290° C., not less than 1.602;
At 300° C., not less than 1.61.

The volume in cubic centimeters of the sulphonation residue in the fraction 305 to 320° C. shall not be greater than one-tenth of the weight in grams of the fraction.

Heavy, high-boiling oils only are suitable for open-tank method of treatment, and are also better preservatives. It was customary to specify from 8 to 10 per cent tar acids, but this is not a part of the above Forest Service specifications. There seems to be no doubt that the phenols aid in the preservation of wood by coagulating the albumen, but they do not remain as long in the wood as the higher boiling and solid compounds, such as naphthalene.

Examination of Pitch. Owing to its complex composition and the little that is known about its constituents, the tests that are applied to it are designed to show the relation of certain physical properties in different samples, and are therefore mostly physical. They include specific gravity, evaporation, melting-point, softening-point, breaking-point, slide test and free carbon determination.

The free carbon is determined in the same manner as for tar, the pitch being made into strings before weighing to present a large surface to action of the solvents.

The evaporation is determined by heating in an air bath at 160° C. for seven hours. Ten grams are weighed into a metal dish similar to those used in milk analysis and the loss in weight noted.

The breaking-point is found by fastening several small pieces of pitch to a copper plate by carefully heating it so that the pitch melts slightly and adheres firmly. It is then placed in tepid water and allowed to remain five minutes to acquire the temperature of the water. The point of a small knife blade is slid along the plate till it touches the pitch, then slowly and forcibly raised, edge first, through it. If the pitch is still soft the blade will be shoved through without scaling off any of the pitch.

The temperature is lowered after each trial by the addition of cold water; after standing five minutes the blade is forced through it again.

If the breaking-point is reached the pitch will scale off with a conchoidal fracture.

Melting-point. The apparatus consists of a mold for making $\frac{1}{2}$-in. cubes of pitch, a beaker of about 600 c.c. capacity, supported on a piece of asbestos board, a thermometer graduated in degrees. Several wires are bent as shown in the cut so as to support the cube of pitch being tested, which is exactly 1 in. from the bottom of the beaker, and a Bunsen burner is so adjusted that the temperature of the liquid in the beaker will be raised 5° C. each minute.

For soft and medium pitches melting below 90° C., distilled water is the bath in which the cube is suspended, but for higher melting-points glycerine, cotton-seed oil, or calcium chloride solution are suitable liquids. Several cubes are supported in the bath so that the under side of each is exactly 1 in. from the bottom of the beaker. A cube is taken out from time to time and twisted with tongs; when one can be readily twisted completely around twice without breaking the softening-point is reached. The melting-point is noted when the cube of pitch drops and just touches the bottom of the beaker. The bulb of the thermometer should be so placed that the bottom of it is at the same height as the bottom of the cube. In the case of low melting-point pitch it is advisable to allow the cube to rest in the bath for five minutes before applying the heat. This method will give duplicates with not more than 2 or 3° maximum variation, even when made by different operators.

The slide or flow test, together with the melting- and breaking-points, is designed to give information of the relative fitness of pitches for roofing purposes. A $\frac{1}{2}$-in. cube of pitch is fastened to a grooved copper plate by slightly heating the plate. The plate is then inclined at an angle of 30°, and placed in an air bath kept at exactly 40° C. for twelve hours. The length of the stream of pitch is measured and compared with other samples known to be satisfactory under given conditions. It is quite important that the slide be insulated by asbestos board from the metal of the oven and that the temperature be maintained at exactly 40° C., as slight variations in the temperature will render the results

valueless. The grooved plate has several grooves and it is customary to test several samples at once.

The specific gravity of pitch is determined in any manner satisfactory for solids. The weighing bottle previously described for tar will be found a very good substitute for the ordinary specific gravity bottle for this work.

The Examination of Light Oil, Crude Naphthas, and Refined Benzols. The usual requirements of the examination of light oil are met by the tests prescribed for the fraction of the distillate from tar up to 200° C., but occasionally it is desirable to determine approximately the constituents of the oil and a larger sample, frequently two to four liters, is worked as follows.

The tar acids and pyridines are removed, the former by caustic soda as previously described under the examination of tar, and the pyridines by dilute sulphuric acid, sp.gr. 1.15. The acid solution from the pyridine extraction is heated on a steam bath, water being added from time to time, to replace that lost by evaporation, till the addition of water no longer produces a cloudiness. The bases are then set free by strong caustic soda solution and their volume measured.

If it is desired, the bases suitable for denaturing alcohol can be determined by distilling the above alkaline solution and separated bases until no further trace of pyridine comes over with the distillate.

The distillate is mixed with four times its volume of absolute alcohol. 10 c.c. of this solution is further diluted with 50 c.c. absolute alcohol and agitated with 2 c.c. of a concentrated aqueous solution of cadmium chloride. After twenty-four hours the crystals that have formed are transferred to a tared filter, dried at 100° C., and weighed. The dry crystals contain 46 per cent of pyridine bases that comply with the specifications for denaturing alcohol.

After the phenols and pyridines have been removed, 1000 c.c. of the extracted oil is distilled in a 2000 c.c. copper still, similar in design to those used for tar testing. The still is fitted with a 6-bulb Lebel-Henninger fractioning tube with copper or platinum gauze in the bottom of each bulb to aid in mingling thoroughly the vapor and condensate. The thermometer is adjusted so that the top of the bulb is level with the side tube. Connection is made to a Liebig condenser or one like those described under tar testing and the distillation carried on at the rate of 2 to 3 drops per second.

Fractions are taken

Up to 75° C., low-boiling, unsaturated bodies and some benzene.
75 to 95° C., crude, 90 per cent benzol.
95 to 105° C., intermediate fraction distilling 60–65 to 100° C.
105 to 125° C., crude toluol.
125 to 170° C., crude solvent naphtha boiling 90 per cent to 160° C.
170 to 200° C., crude heavy naphtha boiling about 80–90 per cent to 200° C.

These fractions, except the last, are shaken in a separatory funnel with 1 per cent of concentrated sulphuric acid in two portions. Each portion is vigorously agitated for five minutes and the settled acid tar carefully drawn off. After the second treatment with acid the oil is washed twice with water, then with caustic soda solution 1.116 sp.gr. and finally with water again. The final traces of water may be removed by passing through a dry filter and a distillation made as described below. The distillations are compared with Tables I, II, III, and IV, from which the approximate yield of the various constituents can be computed.

Mr. G. E. Davis uses the following tables for estimating the probable yield of 50 and 90 per cent benzol and toluol in naphthas.

The distillation of crude and refined benzols is conducted in a 200 c.c. distilling flask with the side tube at the middle of the neck, using 100 c.c. of the sample. The flask should be supported on a 6-in. square sheet of $\frac{1}{8}$-in. asbestos board in which is cut a circular hole not over 1 in. in diameter.

The asbestos sheet prevents superheating the vapors by radiation when the distillation is ending. In distilling high-boiling oils the bulb of the flask above the supporting sheet of asbestos board should be covered by a box of sheet asbestos to protect the bulb from drafts of cold air. A Bunsen burner is the best source of heat. The thermometer is adjusted with the bulb just below the side tube.

The distillation is conducted at the rate of about two drops per second, so that the whole 100 c.c. distills in 20 to 25 minutes. The first drop falling from the condenser is noted as 1 c.c. and the amount collected at each 5° is noted. For the ordinary commercial benzols a thermometer graduated in degrees is satisfactory, but for pure benzol and toluol the graduations should be $\frac{1}{10}$ degrees centigrade. Commercial benzols may contain sulphurous acid set free from unstable compounds formed in washing. A strip of moistened iodate of starch paper may be hung at the mouth of the condenser to detect it.

The barometer materially influences the boiling-point of pure benzol, toluol, and xylol, and a correction of the observed thermometric reading must be made by adding if below 760 mm. and subtracting if above that pressure the product of the difference in millimeters from the standard barometric pressure by one of the following factors: for pure benzene, 0.043, for toluene, 0.047, and for xylene, 0.052.

The test for the amount of acid washing of refined benzol is made by shaking vigorously and thoroughly approximately 7 c.c. of 96 per cent C.P. sulphuric acid with approximately 21 c.c. of the oil to be tested for 15 to 20 seconds in a 1-ounce French square, flint glass, glass-stoppered bottle, allowing to stand for 15 minutes for all grades of refined benzols except refined solvent naphtha and refined heavy solvent naphtha which later are allowed to stand only 5 minutes before

I.—MIXTURES OF BENZENE AND TOLUENE

(Showing the distillation of definite mixtures)

Benzene...	95	90	85	80	75	70	65	60	55	50	45	40	35	30	25	20	15	10	5	Benzene
Toluene...	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80_2	85	90	95	Toluene
81° C.	1																			81° C.
82° "	6	2																		82° "
83° "	65	15	2	1																83° "
84° "																				84° "
85° "	87	70	40	8	1															85° "
86° "						1	1													86° "
87° "								1												87° "
88° "									1											88° "
89° "																				89° "
90° "	95	90	82	74	62	49	37	21	7	1										90° "
91° "											1									91° "
92° "												1								92° "
93° "													1							93° "
94° "														1						94° "
95° "	97	94	91	87	79	75	69	61	51	38	24	7	2							95° "
96° "															1					96° "
97° "																				97° "
98° "	dry																			98° "
99° "																				99° "
100° "		96	94	92	88	85	82	77	72	65	57	48	37	25	8	1				100° "
101° "																	1			101° "
102° "																				102° "
103° "																				103° "
104° "																		1		104° "
105° "		dry	96	95	93	91	89	87	84	80	77	71	67	60	50	39	21	2		105° "
106° "																			1	106° "
107° "																				107° "
108° "			dry																	108° "
109° "				dry																109° "
110° "					96	96	95	94	93	92	91	90	88	87	86	84	80	72	53	110° "
111° "					dry	dry	dry	dry	dry	97	96	95	95	95	95	95	95	95	95	111° "
112° "										dry	dry	dry	dry	dry	dry	dry	dry	dry	dry	112° "

II.—MIXTURES OF TOLUENE AND XYLENE

(Showing the distillation of definite mixtures)

Xylene...	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	Xylene
Toluene...	95	90	85	80	75	70	65	60	55	50	45	40	35	30	25	20	15	10	5	Toluene
111° C.	1																			111° C.
112° "		1																		112° "
113° "			1																	113° "
114° "				1																114° "
115° "	89	69			1															115° "
116° "						1														116° "
117° "							1													117° "
118° "								1												118° "
119° "									1											119° "
120° "	96	92	83	73	61	46	27			1										120° "
121° "																				121° "
122° "											1									122° "
123° "												1								123° "
125° "	dry	96	92	88	83	77	70	60	50	37			1							125° "
126° "														1						126° "
127° "															1					127° "
128° "																				128° "
129° "																				129° "
130° "			95	93	91	88	85	80	76	69	64	54	43	30	15	2				130° "
132° "		dry															1			132° "
134° "																		1		134° "
135° "			96	95	95	93	92	90	87	85	85	81	76	71	61	48	30	8		135° "
136° "																			1	136° "
137° "			dry																	137° "
138° "				dry	96	95	95	94	93	90	90	89	87	86	82	76	68	56	30	138° "
139° "					dry														56	139° "
140° "						97	96	96	95	95	95	95	94	93	92	91	88	84	84	140° "
141° "						dry	dry										95	95	95	141° "
142° "								dry	dry	dry	dry	dry	dry	dry	dry	dry	dry	dry	dry	142° "

III.—MIXTURES OF BENZENE, TOLUENE, AND XYLENE

(Showing the distillation of definite mixtures)

Benzene	80	75	70	65	60	55	50	45	40	35	30	25	20	40	35	30	25	20	Benzene
Toluene	10	15	20	25	30	35	40	45	50	55	60	65	70	40	45	50	55	60	Toluene
Xylene	10	10	10	10	10	10	10	10	10	10	10	10	10	20	20	20	20	20	Xylene
81° C.	1																		81° C.
82° "		1																	82° "
83° "			1																83° "
84° "				1															84° "
85° "	31	7	6	2	1	1													85° "
86° "																			86° "
87° "							1												87° "
88° "																			88° "
89° "																			89° "
90° "	68	56	45	37	19	18	6	1											90° "
91° "									1					1					91° "
92° "										1					1				92° "
93° "																			93° "
94° "											1								94° "
95° "	79	74	68	64	53	48	37	23	12	4	2	1		11	5	1			95° "
96° "													1				1		96° "
98° "																			98° "
100° "	84	80	78	75	69	65	59	51	43	34	22	13	3	35	25	17	6	1	100° "
105° "	87	84	83	81	78	75	72	69	64	59	52	44	33	54	47	40	33	19	105° "
110° "	89	87	86	86	83	82	80	80	77	75	72	68	68	66	63	59	54	47	110° "
115° "	90	88	89	90	88	87	87	87	86	87	86	86	87	76	74	73	72	69	115° "
120° "	91	90	91	91	91	91	92	93	93	94	95	94	95	83	82	83	83	84	120° "
125° "	93	92	93	94	93	94	94	95	95	97	97	97	98	89	89	90	90	91	125° "
130° "	94	94	95	96	96	96	97	98	97	98	98	98	99	94	93	95	95	95	130° "
131° "													dry						131° "
132° "																			132° "
133° "					dry	dry		dry	dry	dry	dry	dry							133° "
134° "		dry	dry				dry												134° "
135° "				dry										97	96	98	98	97	135° "
136° "	dry																		136° "
137° "																dry		dry	137° "
138° "														dry	dry		dry		138° "

IV

MIXTURES OF TOLUENE AND SOLVENT NAPHTHA

(Showing the distillation of definite mixtures)

Toluene	90	80	70	60	50	40	30	20	10	Toluene
Solvent	10	20	30	40	50	60	70	80	90	Solvent
110° C.	1	.....	.....	.....	.....	.....	.....	.....	.....	110° C.
111° "	.....	1	.....	.....	.....	.....	.....	.....	.....	111° "
112° "	.....	.....	1	.....	.....	.....	.....	.....	.....	112° "
114° "	.....	.....	.....	1	.....	.....	.....	.....	.....	114° "
115° "	82	46	26	3	.....	.....	.....	.....	.....	115° "
117° "	.....	.....	.....	.....	1	.....	.....	.....	.....	117° "
119° "	.....	.....	.....	.....	.....	1	.....	.....	.....	119° "
120° "	93	79	66	42	23	2	1	.....	.....	120° "
122° "	.....	.....	.....	.....	.....	.....	.....	1	.....	122° "
125° "	95	89	80	64	52	34	27	4	1	125° "
130° "	96	91	85	77	69	55	42	27	13	130° "
135° "	97	93	89	83	78	70	60	53	34	135° "
140° "	.....	94	91	87	84	77	70	64	55	140° "
145° "	98	95	93	90	88	88	79	75	70	145° "
148° "	dry	.....	.....	.....	.....	.....	.....	.....	.....	148° "
150° "	.....	96	94	92	91	89	85	85	80	150° "
155° "	.....	97	95	94	94	92	90	89	87	155° "
159° "	.....	dry	.....	.....	.....	.....	.....	.....	.....	159° "
160° "	.....	.....	96	95	96	95	93	94	92	160° "
165° "	.....	.....	.....	96	97	97	95	96	94	165° "
166° "	.....	.....	dry	.....	.....	.....	.....	.....	.....	166° "
169° "	.....	.....	.....	dry	.....	.....	.....	.....	.....	169° "
170° "	.....	.....	.....	.....	.....	98	97	97	96	170° "
172° "	.....	.....	.....	.....	dry	.....	.....	.....	.....	172° "
174° "	.....	.....	.....	.....	.....	dry	.....	.....	.....	174° "
175° "	.....	.....	.....	.....	.....	.....	99	98	98	175° "
177° "	.....	.....	.....	.....	.....	.....	dry	.....	.....	177° "
178° "	.....	.....	.....	.....	.....	.....	.....	dry	dry	178° "

being compared with the standard solutions contained in bottles described above.

The tar production of the world was summarized, in an article by Russig in the *Chemische Zeitschrift*, as 1,899,400 tons in 1900, exclusive

	1900	1905
Coal gas tar	60,900 tons	77,643 tons
Coke oven tar	47,500 "	131,117 "
Water gas tar	342,306 "	259,934 "
The census also reports as used:		
Coal tar	110,323 "	127,732 "
Water gas tar	.....	117,459 "
There were imported:		
Crude tar and pitch	80,047 barrels	46,057 barrels
Estimated to equal in tons	18,341	12,722

MIXTURES OF 90% WITH 50% BENZOL

By G. E. Davis

Percentage of 90% Benzol.	Percentage of 50% Benzol.	First Drop.	Per Cent at 100° C.	Per Cent at 120° C.
0	100	92° C.	50	90
5	95	92° "	51	92
10	90	91° "	51.5	92
15	85	91° "	53	92
20	80	90° "	55	92
25	75	90° "	60	93
30	70	90° "	65	93
35	65	90° "	67	94
40	60	88° "	69	94
45	55	88° "	70	94
50	50	87° "	71	94
55	45	87° "	73	94
60	40	86° "	76	95
65	35	86° "	78	95
70	30	86° "	79	96
75	25	85° "	84	96
80	20	85° "	84	97
85	15	84° "	86	97
90	10	84° "	88	dry
95	5	84° "	89	dry
100	0	84° "	90	dry

MIXTURES OF 90% BENZOL WITH COMMERCIAL TOLUOL

By G. E. Davis

Per Cent of 90% Benzol.	Per Cent Toluol.	First Drop.	Per Cent at 100° C.	Per Cent at 105° C.	Per Cent at 110° C.	Per Cent at 120° C.
0	100	103°	0	7	50	94
5	95	102°	0	21	59	94
10	90	101°	0	30	66	94
15	85	100°	0	38	68	95
20	80	97°	9	43	73	95
25	75	95°	16	53	76	95
30	70	95°	23	59	78	96
35	65	94°	43	60	80	96
40	60	93°	43	66	82	96
45	55	92°	46	71	85	97
50	50	91°	52	72	86	97
55	45	91°	58	76	86	97
60	40	91°	60	78	88	97
65	35	90°	65	81	89	97
70	30	89°	71	83	91	97
75	25	88°	75	85	91	98
80	20	87°	77	87	92	98
85	15	86°	83	89	93	98
90	10	85°	85	91	94	dry
95	5	84°	88	93	95	dry
100	0	84°	90	94	96	dry

MIXTURES OF 50% BENZOL WITH COMMERCIAL TOLUOL

By G. E. Davis

Per Cent 50% Benzol.	Per Cent Toluol.	First Drop.	Per Cent at 100° C.	Per Cent at 105° C.	Per Cent at 110° C.	Per Cent at 120° C.
100	0	92°	50	68	80	91
95	5	93°	45	64	76	91
90	10	94°	33	60	73	90
85	15	94°	30	58	73	90
80	20	95°	28	57	72	90
75	25	95°	26	55	71	90
70	30	96°	22	48	67	90
65	35	96°	19	47	65	90
60	40	96°	15	46	65	90
55	45	97°	12	44	65	90
50	50	98°	8	42	64	90
45	55	98°	4	34	57	90
40	60	99°	0	26	56	90
35	65	100°	0	25	55	90
30	70	100°	0	23	53	90
25	75	100°	0	21	53	90
20	80	100°	0	16	48	90
15	85	101°	0	14	46	90
10	90	102°	0	13	45	90
5	95	103°	0	10	44	90
0	100	103°	0	0	39	90

of blast-furnace and water-gas tars. In the table given on the bottom of page 585, the U. S. Census reports the production of the United States.

Statements have been made that only 20 to 30 per cent of the tar produced in the United States was taken by the tar distillers. From the above figures it would seem that all of the coal tar and a large portion of the water-gas tar was used by the distillers.

CHAPTER XXII

THE PETROLEUM INDUSTRY

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Petroleum. Petroleum, from two Latin words: *Petra*, a rock, and *Oleum*, oil, is an inflammable oily liquid of characteristic odor, generally found in large quantities in porous rocks called sandstones—of practically all geological ages of the earth's crust from the Lower Silurian to the latter part of the Tertiary, and is usually overlaid by an impervious formation. In appearance it varies widely, some being found of light yellow color and very limpid, while others are almost black and of high viscosity. The specific gravity, according to Redwood,[1] varies from 0.771 to 1.06 (51.5 to 2.3° Beaumé).

The occurrence of petroleum has been known since 450 B.C.[2] at Kirab, in Persia. The early settlers in America found the Seneca Indians gathering it from what is now Oil Creek, near Oil City, Pennsylvania. It was also associated with the brine from the salt wells of the Kanawha Valley in West Virginia.

Mr. George H. Bissell, a New York lawyer, was the first man to propose drilling for oil, and in 1858 the Seneca Oil Co., organized by him, engaged the services of Mr. E. L. Drake as superintendent, and started operations on a plot of ground leased from the Pennsylvania Rock Oil Company. After many delays they were finally rewarded by striking a 25-barrel[3] well at a depth of 69 ft., in August, 1859. This marked the beginning of the petroleum industry.

Origin of Petroleum. The origin[4] of petroleum has been the subject of much discussion among scientists throughout the world, the theories set forth being divided into two groups the inorganic and the organic. The inorganic theories consider petroleum to have been produced by the reaction of inorganic substances. Berthelot believed it to have been formed by the action of steam and carbon dioxide on highly heated alkali metals, which, according to Daubree's hypothesis, were supposed to exist in the

[1] "Petroleum and its Products," by Sir Boverton Redwood.

[2] The early writings of Herodotus; Bibliography of the Annual Report of the Geo. Survey of Penna., 1886.

[3] A well yielding twenty-five 42-gallon barrels per day.

[4] For a more detailed description of the origin of petroleum, the reader is referred to "Petroleum and its Products," Vol. I, Sir Boverton Redwood.

depths of the earth. Mendelejeff believed it to have been formed by the action of water on highly heated metallic carbides. These theories have been supported by laboratory experiments, yet they are not in accord with the geological conditions under which petroleum is found.

The organic theories that petroleum has resulted from the decomposition of either animal or vegetable matter, or both, comply more fully with the views held by the geologists, and have also been supported by laboratory experiments. Peckham [1] believed that petroleum was produced by the slow distillation of animal and vegetable matter at a low temperature; Phillips [2] and Sterry Hunt,[3] that it was due to the decomposition of vegetable matter under water and in the absence of air. Orton [4] considered Pennsylvania petroleum to have been derived from organic matter of bituminous shale, probably vegetable; and Canadian oil produced from limestone, probably animal.

Constitution. Crude petroleum consists essentially of a complex mixture of hydrocarbons of different boiling points, often accompanied by small percentages of oxygen, sulphur, and nitrogen compounds. The oils produced from different localities often vary widely in chemical composition, but they are all refined by the same general methods.

The following table [5] given by F. W. Bushong shows the ultimate chemical composition of samples obtained from different localities:

Sp.Gr.	Field.	Carbon.	Hydrogen.	Sulphur.	Nitrogen.
.....	Pennsylvania (235).....	86.06	13.89	0.06	....
0.8095	Oil City, Pa. (236).....	85.80	14.04	....	....
0.8367	Welker, Ohio (236).....	85.46	13.91	0.48	....
0.836	Findlay, Ohio (236).....	84.57	13.62	0.72	0.11
0.862	Petrolia, Canada (236).....	83.94	13.37	0.99	....
0.865	Cherryvale, Kan. (237).....	85.43	13.07	0.37	....
.....	Baku, Russia (235).....	86.25	13.48	....	....
0.912	Humboldt, Kan. (237).....	85.63	12.44	0.37	....
0.912	Beaumont, Tex. (238).....	85.05	12.30	1.75	....
0.912	Ventura, Cal. (239).....	84.00	12.70	0.40	1.70
0.940	Humboldt, Kan. (237).....	85.33	11.80	0.15	....
0.9458	McKittrick, Cal. (240).....	86.06	11.45	0.87	....
0.9845	Santa Barbara, Cal. (236)....	86.32	11.70	0.84	....

235 Engler, Ber. d. Deutsch. Chem. Ges., 28, 2501, 1895.
236 Mabery, Amer. Chem. Jr. 17, 713, 1895; 18, 55, 149, 1896; Proc. Amer. Acad. A. and S., 40, 323, 1904.
237 Bartow and McCollum, Trans. Kan. Acad. Sci., 19, 58, 1903.
238 Richardson, Jr. Franklin Inst., 113, 162, 1900.
239 18th Ann. Rep. U. S. G. S., 842, 1896-97.
240 O'Neill, Jr. Amer. Chem. Soc., 25, 699, 1903.

The oil refiner divides petroleum into two general classes, viz.: the "paraffin-base," those yielding solid hydrocarbons of the paraffin series

[1] United States Census Report, 1880.
[2] Phillips Amer. Chem., XVI, p. 429.
[3] Bull. Soc. Geol., XXIV, p. 570.
[4] Report on the occurrence of petroleum, natural gas, and asphalt rock in Western Kentucky, 1892.
[5] University Geol. Survey of Kansas, Vol. IX, 1908.

C_nH_{2n+2}; and the "asphaltic-base," or those rich in asphalt and containing practically no solid paraffins. There is, however, no sharp line of distinction, as some of the oils from Kansas, Oklahoma, Northern Texas, and Illinois contain both asphalt and paraffin.

Locality. The oil from Pennsylvania, of the Appalachian field, which includes Pennsylvania, New York, Southeastern Ohio, West Virginia, and Kentucky, is generally considered the best grade of petroleum produced in large quantities. This is a "paraffin-base" oil, but contains small quantities of the olefin series C_nH_{2n}, the benzene series C_nH_{2n-6}, and traces of the naphthene series, which are hydrogen addition products of the benzene series, and isomeric with the olefin series. The color by transmitted light varies from amber to red, and by reflected light is green, due to the so-called "bloom" or fluorescence. In specific gravity it ranges generally from .8641 to 7821 (32.0 to 49.0° Beaumé). It contains very little sulphur (.06 to .084), practically no asphaltic matter, and gives a good yield of gasoline, illuminating oils, and paraffin wax.

The Canadian oil and that from Lima, Ohio, are also paraffin-base oils; but as they are high in sulphur (Lima[1] oil 0.6 per cent, and Petrolia, Canada,[1] 0.98 per cent), the illuminating oils separa ed from them have to be desulphurized in order to make them merchantable.

The petroleum from Illinois is lower in sulphur (.25 per cent to .32 per cent), much of it being refined without special treatment; but that from some pools contains asphalt as well as solid paraffin, as do some from Kansas, Oklahoma, and Northern Texas.

The California[2] oils are of the asphaltic type and are made up of a large proportion of nitrogen bases of the pyridin, or hydropyridian, and chinolin type. They also contain members of the terpene series, C_nH_{2n-4}, and the benzene series, C_nH_{2n-6}, as does the oil from Beaumont, Texas.

There are small quantities of petroleum produced in Pennsylvania, West Virginia, and other localities, which possess lubricating qualities in their natural state, and need only to be strained before they are placed on the market; but, as the production is small, these oils are only of passing interest.

Of the other countries, Russia is the largest producer. The oil from Baku differs chemically from the Pennsylvania oil in being made up largely of the "naphthene" series, which, according to Markownikow[3] and and Ogloblin, constitutes 80 per cent.

Smaller fields exist in Sumatra, Java, Borneo, Galicia, Roumania, Egypt, Persia, Africa, India, Japan, Mexico, Germany, Peru, and Italy.

The following tables give the rank of the petroleum producing countries, with the quantity produced and the percentage of each in 1915, and since 1857:

[1] Mabery.
[2] Prof. F. W. Bushong, Univ. Kansas Bull. Vol. IX, p. 307.
[3] Jour. Chem. Soc. XLII, 390; XLVI, 1276.

WORLD'S PRODUCTION OF CRUDE PETROLEUM, IN 1915 AND SINCE 1857, BY COUNTRIES [1]

Barrels of 42 gallons

Country.	Production, 1915.			Total Production, 1857–1915.		
	Barrels of 42 gallons.	Metric tons.	Percentage of total.	Barrels of 42 gallons.	Metric tons.	Percentage of total.
United States...	*a*281,104,104	*a*37,480,547	65.73	*a*3,616,561,244	*a*482,208,266	60.09
Russia.....	68,548,062	9,353,077	16.03	1,690,781,907	222,984,256	28.09
Mexico.....	32,910,508	4,388,068	7.69	123,270,377	16,420,008	2.05
Dutch E. Indies*b*	12,386,808	1,710,445	2.90	148,999,921	20,087,939	2.48
Roumania.....	12,029,913	1,673,145	2.81	130,012,387	17,477,878	2.16
India.....	8,202,674	1,093,690	1.92	81,592,385	10,878,984	1.36
Galicia.....	4,158,899	578,388	.97	136,032,500	18,918,364	2.26
Japan and Formosa.....	3,118,464	415,785	.73	30,169,622	4,022,606	.50
Peru.....	2,487,251	331,633	.58	16,794,223	2,239,229	.28
Germany.....	995,764	*c*140,000	.23	13,961,333	1,875,974	.23
Trinidad.....	*c*750,000	100,000	.18	2,819,430	375,924	.05
Argentina.....	516,120	75,900	.12	1,033,121	151,693	.02
Egypt.....	221,768	29,569	.05	1,308,496	174,466	.02
Canada.....	215,464	28,729	.05	23,709,074	3,161,210	.39
Italy.....	39,548	*c*5,500	.01	842,020	119,279	.01
Other countries..	*c*10,000	1,333		372,000	49,600	.01
	427,695,347	57,405,809	100.00	6,018,260,040	801,145,676	100.00

a Marketed production. *b* Includes British Borneo. *c* Estimated.

Production. Crude petroleum is obtained by drilling through the overlying strata to the oil producing sands beneath, proceeding in practically the same manner as in boring an artesian water well. The depth of the wells depend on the locality. In Pennsylvania the depth varies from 300 to 3700[2] ft. It sometimes happens in drilling, when the oil bearing stratum is tapped, that the oil rushes out of the well with great force, due to confined gas; such a well is called a "gusher." Some of the big gushing wells of Russia have started producing at the rate of 200,000 barrels of oil per day. The famous Lucas well struck at Spindle Top near Beaumont, Texas, on Jan. 10, 1891, at a depth of from 1029 to 1069 ft., is estimated to have started gushing at the rate of 70,000 barrels per day, and probably flowed 500,000 barrels before it could be capped.

[1] "Petroleum in 1915," by John D. Northrop, Dept. of the Interior, U. S. Geological Survey.

[2] "Petroleum and its Products," by Sir Boverton Redwood.

Although we are producing more oil now than ever before, owing to the development of new fields, the older fields are slowly diminishing in production. According to the U. S. Geol. Report for 1912, Pennsylvania, in 1891, produced 33,009,236 barrels, and Texas, in 1905, produced 28,136,189 barrels; Pennsylvania, in 1912, produced only ,837,948, and Texas, 11,735,057 barrels.

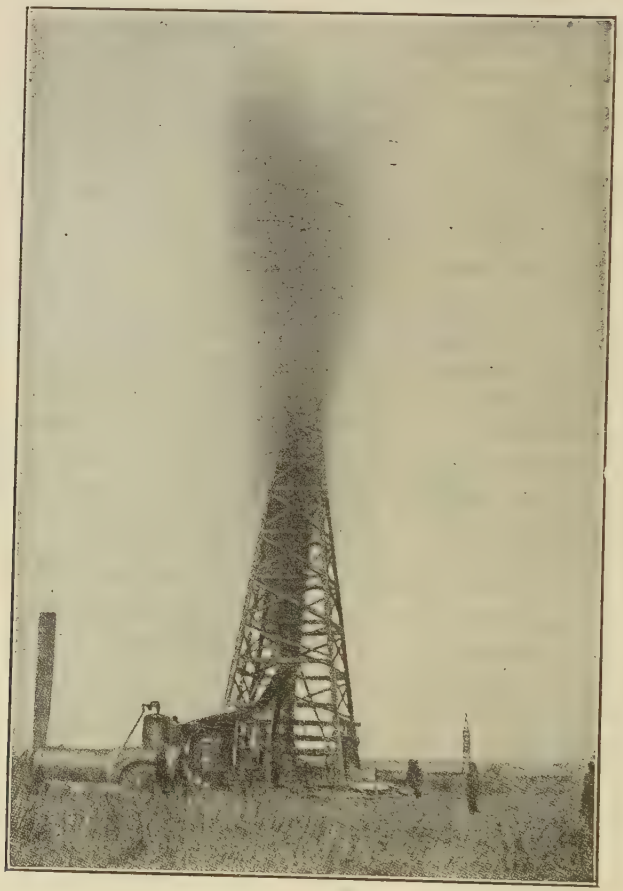


Fig. 249.

The production of a well is sometimes increased by "shooting," i.e., by exploding a shell of nitro-glycerine in the producing zone. Photograph, Fig. 249, shows a well spouting after being shot.

As the Pennsylvania petroleum is of excellent quality, it is found profitable to pump wells yielding only one-fourth barrel per day; such wells are connected in series and worked as a unit.

[1] U. S. Geol. Survey Bull. "The Production of Petroleum in 1902," F. H. Oliphant.

The petroleum as produced is always accompanied to a greater or less degree by water and B. S. (bottom settlings). The water is removed by settling, and also the B. S., if it is earthy matter, or inert organic matter;

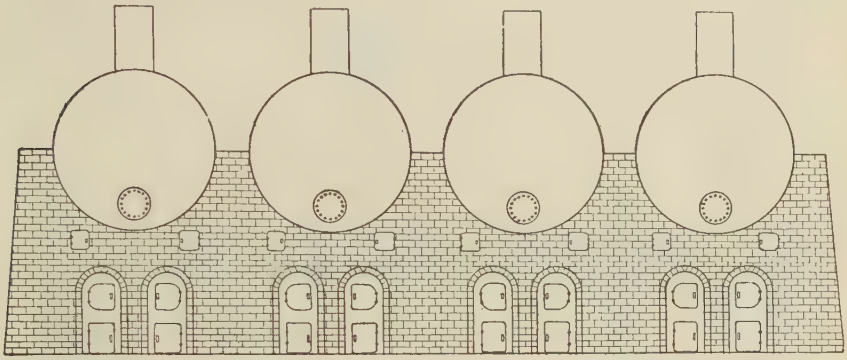


FIG. 250.

but in case of Pennsylvania petroleum, where it is principally an emulsion of amorphous paraffin wax and water, it is refined with the crude oil after the water has been separated.

Petroleum is transported great distances from the fields to the storage tanks (30,000 to 75,000 barrels capacity) of large refineries, through pipe lines of from 4 ins. to 8 ins. in diameter, the average line being 6 ins. The

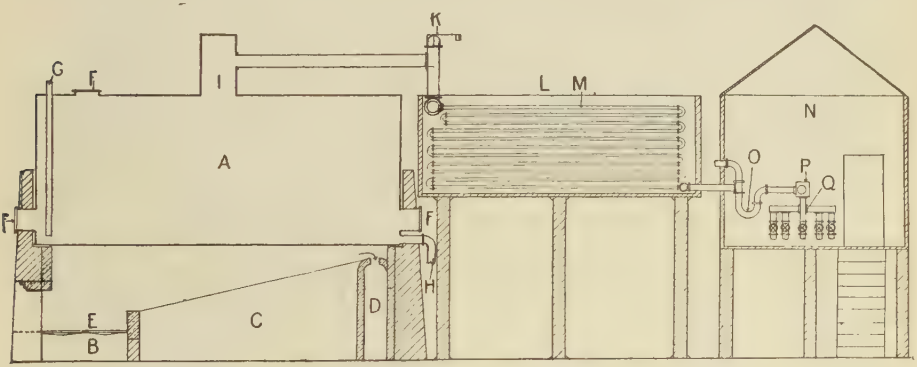


FIG. 251.—*A*. Still; *B*. Ash-pit; *C*. Filling; *D*. Flue; *E*. Fire-box; *F*. Manholes; *G*. Filling line; *H*. Pumping out line; *I*. Dome; *J*. Goose neck; *K*. Safety valve; *L*. Condenser box; *M*. Condenser coil; *N*. Tail house; *O*. Gas trap; *P*. Look-box; *Q*. Manifold.

longest distance known to the writer is from the Oklahoma field, via Kansas City and Chicago, to the seaboard, a distance of about 1600 miles.

Refining. The first step in the separation of petroleum into its various products is fractional distillation, and this is modified according to

the nature of the crude oil, and the products desired. The horizontal steel stills [1] used for this operation vary in construction, but those in gen-

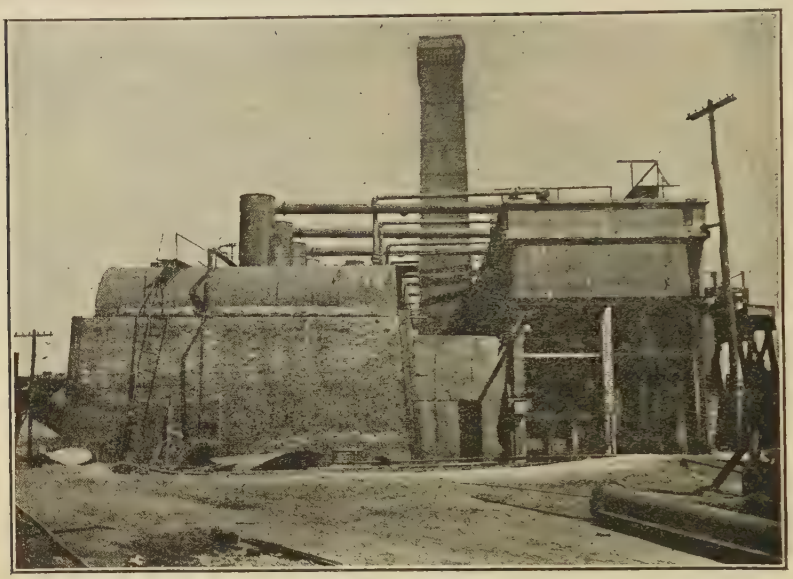


FIG. 252.

eral use in this country [2] are cylindrical steel shells set in brickwork, as shown in Figs. 250 and 251, the upper half being exposed except for an iron jacket covering. The largest stills of this type are about 42 ft. long by 15 ft. in diameter, with a charging capacity of about 1200 (42 gallons) barrels. They may be either end or side fired, the latter being preferable on account of the ease with which the still can be controlled. The fuel used may be either coal or oil, it being cheaper to burn oil in some cases, as in California and Russia, where, owing to the scarcity of coal, oil is used almost entirely.

FIG. 253.

The stills are usually fitted with domes at the top which are connected

[1] Several years ago the "Cheese-box" or upright still were used, but proving expensive to operate and to repair they were discontinued.

[2] In Russia and also slightly in this country horizontal stills with longitudinal flues are used.

with 12 to 16-inch vapor pipes, or " goose necks " that lead to condensers. The condensers consist of coils of pipe set in tanks, through which cold water is circulated. The pipes connecting the condenser coils with the " tail house," some distance away, are called the " running lines," and are usually provided with traps for separating the uncondensed gas which is subjected to pressure in order to separate the light gravity gasoline carried by it The residual gas is utilized in gas engines or burned under the stills. The running lines are intercepted in the " tail house " by " look boxes " enclosed with glass, Fig. 254, so that the "stream " (distillate flowing from the condenser) can be watched by the stillman in charge. The

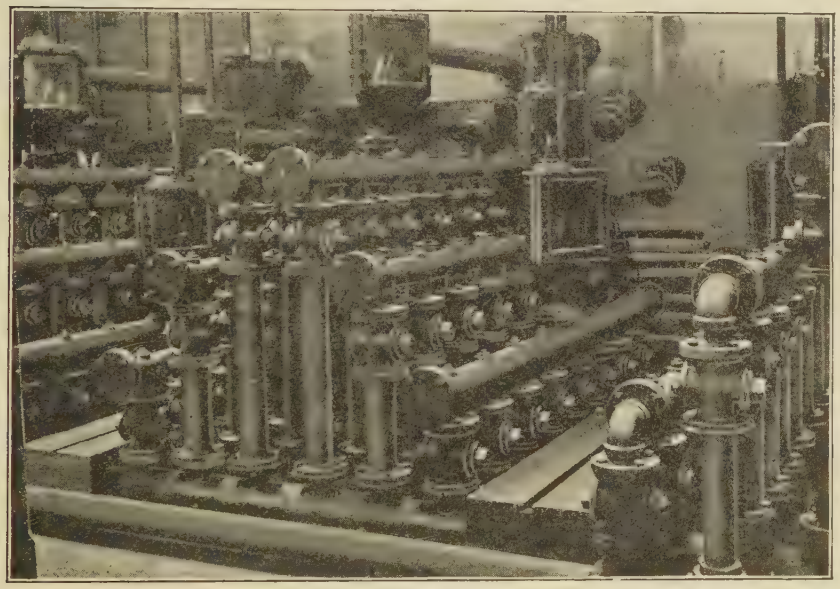


Fig. 254.

look boxes are equipped with small cocks, so that samples can be taken from time to time. The process is usually controlled by the gravity of the stream, or other simple tests made by the stillman. The bottom of the " look box " connects with a manifold usually having cocks or valves, so that the distillate may be run into any receiving tank desired.

In some refineries, several stills are connected and run continuously, by simultaneously charging into the first still slowly, and pumping from the last, each still being fired stronger than the preceding one, so that different boiling point fractions are obtained from each one.

When distilling oil continuously the heat from the reduced oil passing from the last still is transferred to the oil being charged into the first still, by passing the hot and cold oil in opposite directions through an exchanger. The exchanger consists of a system of coils arranged in a steel shell; the

hot oil passing through the coils gives up its heat to the cold oil being pumped through the shell to the still.

As before stated, the method of distilling is dependent on the products desired When petroleum is distilled by means of fire alone, the heavy vapors which condense in the top of the still drop back into the superheated oil, and are thereby partially decomposed. This decomposition, or " cracking," causes oils of lower specific gravity than are normally present to be produced, and is called the " dry," or destructive distillation.

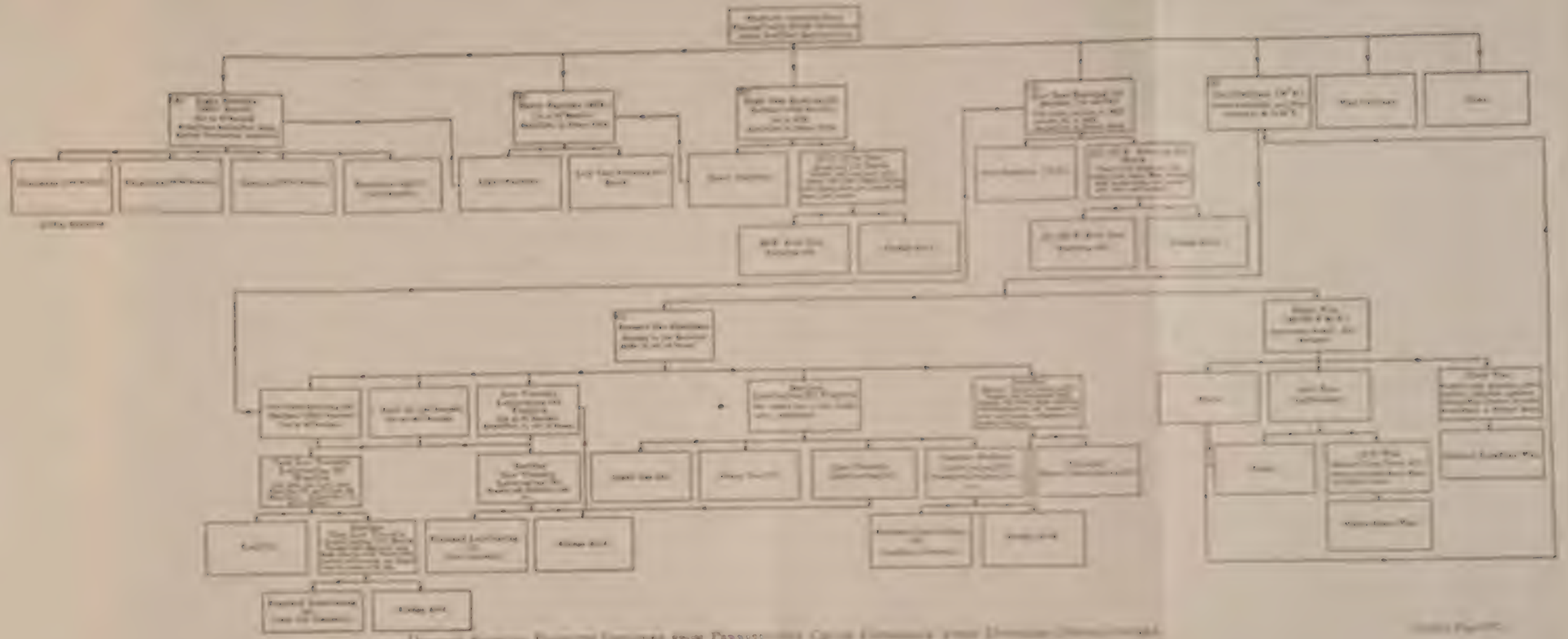
COMPARATIVE TESTS OF THREE DIFFERENT SAMPLES OF CRUDE PETROLEUM, ALSO THE SPECIFIC GRAVITIES, AND COLD TESTS, OF THE FRACTIONS OBTAINED FROM SAME BY DESTRUCTIVE DISTILLATIONS

	Pennsylvania.	Illinois.	Indian Territory.
Color, Sulphur, Specific Gravity	Yellow 0.078% 41.9° Baumé.	Nearly Black, 0.205% 33.8° Baumé.	Dark Green, 0.283% 37.5° Baumé.
Distillation:	% Bé. Gr. ° F.	% Bé. Gr. ° F.	% Bé. Gr. ° F.
First Fraction,	10.0—70.0 —	10.0—60.5 —	10.0—67.9 —
Second "	10.0—58.8 —	10.0—51.5 —	10.0—56.4 —
Third "	10.0—52.8 —	10.0—45.6 —	10.0—50.6 —
Fourth "	10.0—48.1 —	10.0—40.6 —	10.0—45.1 —
Fifth "	10.0—43.7 —	10.0—36.7 —	10.0—40.5 —
Sixth "	10.0—40.2 28 C.T.	10.0—34.3 36 C.T.	10.0—36.6 41 C.T.
Seventh "	10.0—39.3 48 "	10.0—34.2 50 "	10.0—34.2 42 "
Eighth "	10.0—38.9 57 "	10.0—34.6 53 "	10.0—33.9 55 "
Ninth "	10.0—38.8 61 "	10.0—36.8 46 "	10.0—36.6 47 "
Tenth "	8.5—36.9 55 "	6.0—21.3 47 "	5.0—36.9 46 "
Coke and loss	1.5	4.0	5.0
	100.0	100.0	100.0

This method is used when a large percentage of burning oils is desired. The products when running on Pennsylvania, or paraffin-base crude oil, are: naphtha (sometimes redistilled, for cymogene, rhigolene, petroleum spirit and gasolene), burning oils, gas and fuel oils, paraffin lubricating oils, wax and coke. Heretofore the practice has been to first " run " the " crude " to tar (about 9 to 12 per cent residuum) in the crude stills, and to distil the tar separately at the tar stills for paraffin or " tar " distillate (lubricating oil distillate containing the paraffin wax) and coke.

The latest practice is to continue the distillation to coke in " Tower Stills " Without interruption and separate the different raw products in one distillation. The " Tower Still " is so called on account of the tower like aerial condensers connecting with the goose-neck, and interposed between the stills and water cooled condensers. The office of these towers is one of fractional condensation.

They usually consist of a top and bottom gas chamber connected by pipes, around which the air circulates causing partial condensation. The



Prepared by T. T. Gray for Rogers' "Industrial Chemistry"

vapor pipe or goose-neck carrying the hot vapors from the stills connects into the bottom gas chamber of the first tower and travels up through the pipes through the top gas chamber into the bottom of the second tower, and so on through the series to an ordinary water-cooled condenser, consisting of coils of pipes set in a tank of water. The towers and water condenser all connect in the receiving house (tail house) with "look-boxes," enclosed with glass so that the flow of the different streams may be observed and samples can be taken for gravity tests.

The tower still has many advantages over the old style apparatus. Condensation taking place in each tower separates what would otherwise be one product into as many products as there are towers, and therefore reduces further necessary redistillation to a minimum.

When lubricating oils of superior quality, such as spindle and cylinder oils, are being manufactured, it is necessary to prevent the decomposition of the crude oil as much as possible. This is accomplished by introducing steam (dry but not necessarily superheated) into the oil in the still by means of a perforated coil. The atmospheric pressure upon the mixture is divided between the hydrocarbons and the steam and the partial pressure on the hydrocarbons is less than the atmospheric pressure, consequently they distil over at temperatures lower than their normal boiling points. The steam jets also keep the oil in constant state of agitation, thereby preventing it from getting overheated at the bottom of the still next to the fire. This method is called the "steam" distillation; the products are: Naphtha, burning oils (less than when distilled destructively), gas and fuel oils, spindle oils, paraffin wax and cylinder oils. Some refiners use the vacuum distillation, in conjunction with the steam distillation, where, by the aid of a pump, a partial vacuum is created in the still, and the hydrocarbons pass over at temperatures much below their normal boiling points. The vacuum stills are of the same general type as the ordinary horizontal "crude stills," but are smaller and heavier.

Naphtha and Illuminating Oils. The chart facing this page shows the different steps in the "dry" distillation of Pennsylvania crude oil. The "stream" (distillate flowing from the condenser) begins running into the "tail house" under ordinary conditions at about 80° Bé. (.6666 sp.gr); it is practically water white in color, and is "run" into light naphtha (Fraction *A*) until it reaches 69° Bé. (.6965 sp.gr.). From 69 to 58° Bé. (.7035 to .7446 sp.gr.) the distillate is collected as heavy naphtha (Fraction *B*); but as it is more or less contaminated with some of the heavier hydrocarbons of boiling points too high for use as naphtha, it has to be redistilled in a "steam still," (a still heated by steam coils and steam jets). The upper fraction is added to the light naphtha (Fraction *A*), and the residue used for blending with the low test burning oil which follows.

The naphtha Fractions *A* and *B*, representing from 12 to 15 per cent of the crude oil, can be worked up in several different ways. They can

be used for all ordinary purposes without further refining, or may be redistilled, the very volatile fractions being condensed by extreme cold, and under pressure, thereby separating cymogene, rhigolene, gasolene and petroleum spirit, which Allen in his "Commercial Organic Analysis," Vol. II, part I, p. 96, classifies as follows:

Commercial Name.		Degrees Baumé.	Specific Gravity.	Composition.
Cymogene		108	0.588	Consists chiefly of tetrane, C_4H_{10}.
Petroleum Ether	Rhigolene	94 to 92	0.625 to 0.631	Consists chiefly of pentane and isopentane, C_5H_{12}.
	Gasolene (Canadol)	95 to 80	0.622 to 0.666	Consists chiefly of hexane, C_6H_{14} and isohexane.
Petroleum Spirit or Benzolin	C. Naphtha	76 to 70	0.680 to 0.700	
	Benzine-naphtha			
	B. Naphtha	66 to 65	0.714 to 0.718	
	A. Naphtha	59 to 58	0.740 to 0.745	
	Benzin			

In order to improve the odor of the naphtha it is sometimes treated with about two to four pounds of 66° Bé. commercial sulphuric acid per barrel of 50 gallons, by agitation in tall, lead-lined cone-bottomed tanks, Figs. 255 and 256, called agitators, of from 300 to 500 barrels capacity, provided with mechanical stirring gears, in preference to an air blast, in order to prevent loss by evaporation. The acid is allowed to settle and draw off into the sludge acid tank. The naphtha is washed thoroughly with water by means of a spray and finally by agitation with water, and is then made alkaline with caustic soda of 4 to 10° Bé., and finally washed with water until neutral, when it is pumped into tanks and allowed to settle until bright. After this treatment it becomes known as "deodorized naphtha."

To recur to the original distillation, from 58 to 43° (.7446 to .8092 sp.gr.), or as long as the stream runs good color (almost colorless) the high test burning oil (Fraction *C*), is collected. It is "steam stilled" to 150° F. fire test, and the distillate put into heavy naphtha (Fraction *B*). The residue from the steam, still known as 150° W. W. Stock, is treated as described later.

When the distillate begins to go "off color," due to cracking, it is "cut into" low flash burning oil distillate (Fraction *D*), which is also steam stilled, the volatile fraction being naphtha of 70° Bé. (.7000 sp.gr.), called "gas naphtha" from its objectionable odor. Gas naphtha contains a large proportion of unsaturated hydrocarbons, and goes into the cheaper grades of naphtha. The appearance of so low a specific gravity fraction at this stage of the distillation, illustrates clearly the effect of the "cracking" process.

The burning oil stocks from the steam stills, constituting from 65 to 75 per cent of the crude oil charged, are treated at the rate of 5 to 10 lbs. of 66° commercial sulphuric acid per barrel, in order to improve the color and odor, also to remove decomposition products which cause the flame to smoke when burned in lamps. The process is performed in agitators in much the same manner as with naphtha, only an air blast is used for agitation instead of a stirring gear. In order to get the full benefit of the acid, any water present must first be drawn off, and a small amount of acid added in order to remove all of the remaining water; this is agitated for from 20 to 40 minutes, allowed to settle from the oil

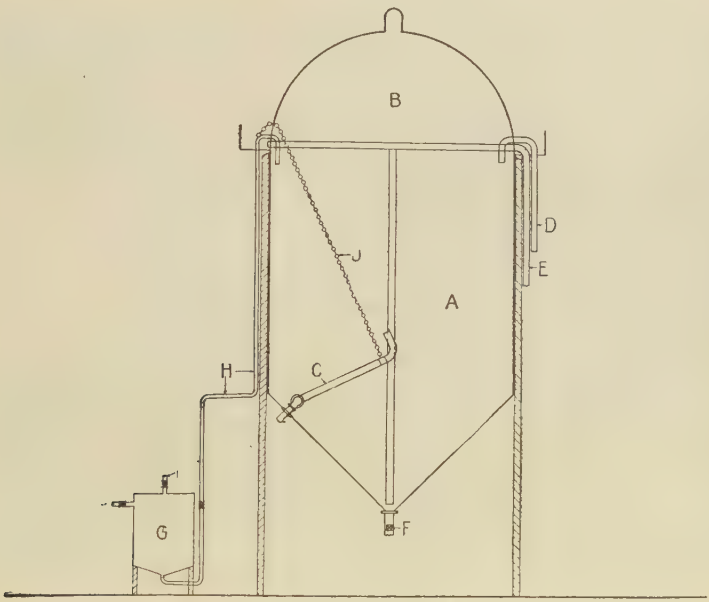


Fig. 255.—*A*. Agitator; *B*. Dome; *C*. Swing suction for pumping out oil; *D*. Oil-filling line; *E*. Air blast; *F*. Cock for drawing off sludge; *G*. Acid tank; *H*. Acid line; *I*. Compressed air line; *J*. Chain for operating swing suction.

and then drawn off. The remaining acid is then added and the mass agitated for from one-half to one hour, allowed to settle from 3 to 5 hours, and drawn off. The acid treatment removes the tarry matter formed during distillation, also a large percentage of the unsaturated hydrocarbons and sulphur compounds. The acid is turned almost black after treatment, and is known as "sludge" acid. The "sludge" acid is allowed to settle from the oil and is then drawn off into tanks and delivered to the acid separating plant for the recovery of the acid, which will be described later. After the separation of the sludge, the oil is washed thoroughly with water, made alkaline with caustic soda of from 4 to 10° Bé. by agitation, and then washed with water until neutral;

the wash water is separated and the oil pumped into settling tanks where it is allowed to settle until bright.

Sulphur Content. Pennsylvania petroleum contains very little sulphur (.06 to .082 per cent), the burning oils made from it therefore requiring no further treatment; but when oils containing considerable sulphur, such as that from Lima, Ohio, Texas, and Canada, are being refined a special desulphurizing is necessary in order to get rid of most of the sulphur compounds which cause charring of the lamp wick, and burn with a smoky flame. There are many processes for affecting this, the two best known being the " litharge " and the " Frasch " methods.

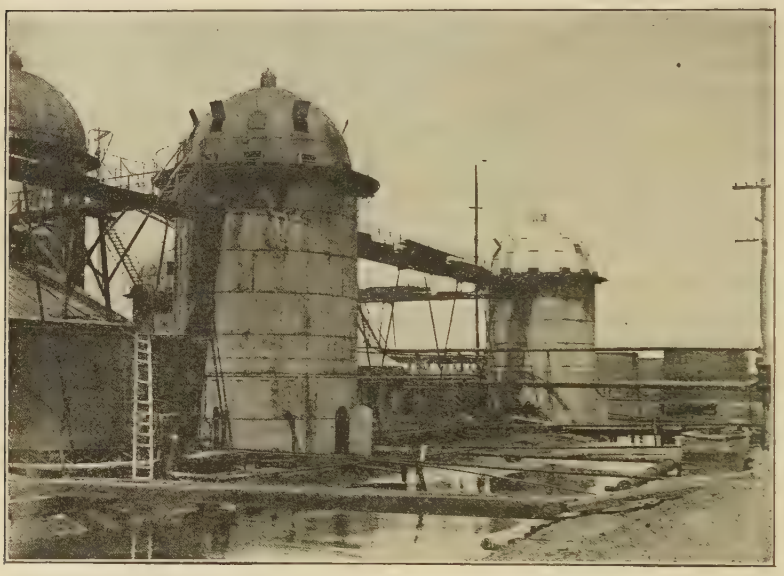


FIG. 256.

The litharge method consists of agitating the oil with a solution of litharge (lead oxide) in caustic soda; the sulphur is precipitated as a lead sulphide and drawn off. Although this method reduces the sulphur considerably, it is not as thorough as the " Frasch " process, where the oil is heated with finely divided copper, or copper oxide in " sweetening " stills provided with heavy stirring gears. The copper sulphide formed is afterwards roasted in order to remove the sulphur and the resulting copper oxide used for the next treatment.

Lubricating Oils. The residue (*E*) from the original distillation of the crude oil (10 to 12 per cent) is known as tar. It is from 21 to 22° Bé., very dark in color and contains the paraffin lubricating oil and wax.

In order to manufacture the lubricating oils known in the trade as " paraffin oils," the tar is first distilled destructively in stills of

practically the same type as the "crude stills," only they are smaller in capacity (250 to 500 barrels). The process is continued until everything has passed over except the coke formed by the destructive distillation. At the latter part of the distillation, just before the still has "coked," a yellow, sticky, semi-asphaltic product passes over which is known as "wax tailings;" on analysis this has been found to contain anthracene, chrysene, and other products formed by the "cracking" process. The bottoms of the stills often get red hot during the coking period. The coke resembles gas coke in appearance, but is more fragile. The yield from tar averages from 10 to 12 per cent, or about 1 per cent from the crude oil, and on account of its purity is used principally for making electric light and battery carbons, and also to some extent in metallurgical processes.

The distillate from tar known as paraffin,[1] or unpressed tar distillate (Fraction *F*),[1] is yellow in color and contains the wax and paraffin lubricating oils. It has a gravity of 30° Bé. (.875 sp.gr.), and a solidifying point of about 70° F. due to the solid paraffins present. It is treated with 66° Bé. commercial sulphuric acid at the rate of 8 to 10 lbs. per barrel in the same manner as the treating of burning oils, the agitator in this case being heated by a steam jacket in order to keep the paraffin distillate liquid. After treatment it is delivered to the pressing plant, where it is chilled down to from 20° to 24° F. in steel shells containing stirring gears called "coolers" provided with jackets through which cold brine is circulated. A refrigerating plant is therefore necessary when refining crude oils containing solid paraffins. When the proper temperature (20° to 24° F.) is reached, it is pumped to a filter press, Fig. 257, which is provided with plates covered with canvas; the oil passes through and drains off, and the wax is held by the canvas. The oil thus expressed is known as pressed tar distillate (Fraction *G*), and the wax separated, containing considerable oil (30 to 40 per cent), known as "slack wax," is removed from the canvas covered plates,[2] by scraping with "spuds," when it is carried by means of conveyors under the press to the "slack wax" tank.

The pressed tar distillate has a cold test (solidifying point) of 20° to 25° F., and is used for making all of the paraffin lubricating oils. It is charged into the "reducing stills," which are the same type as the crude stills, but smaller in capacity (about 300 to 500 barrels); and the upper halves, instead of being exposed, are bricked in. Here it is "steam reduced" according to the test desired, by firing underneath and at the same time introducing steam into the body of the oil by means of a perforated coil placed inside on the bottom of the still. In making high viscosity oils the distillation would naturally be carried further

[1] The general practice now is to separate the paraffin distillate at the crude stills.

[2] The canvas covers of the plates are usually spoken of as "bags," although the term seems misleading.

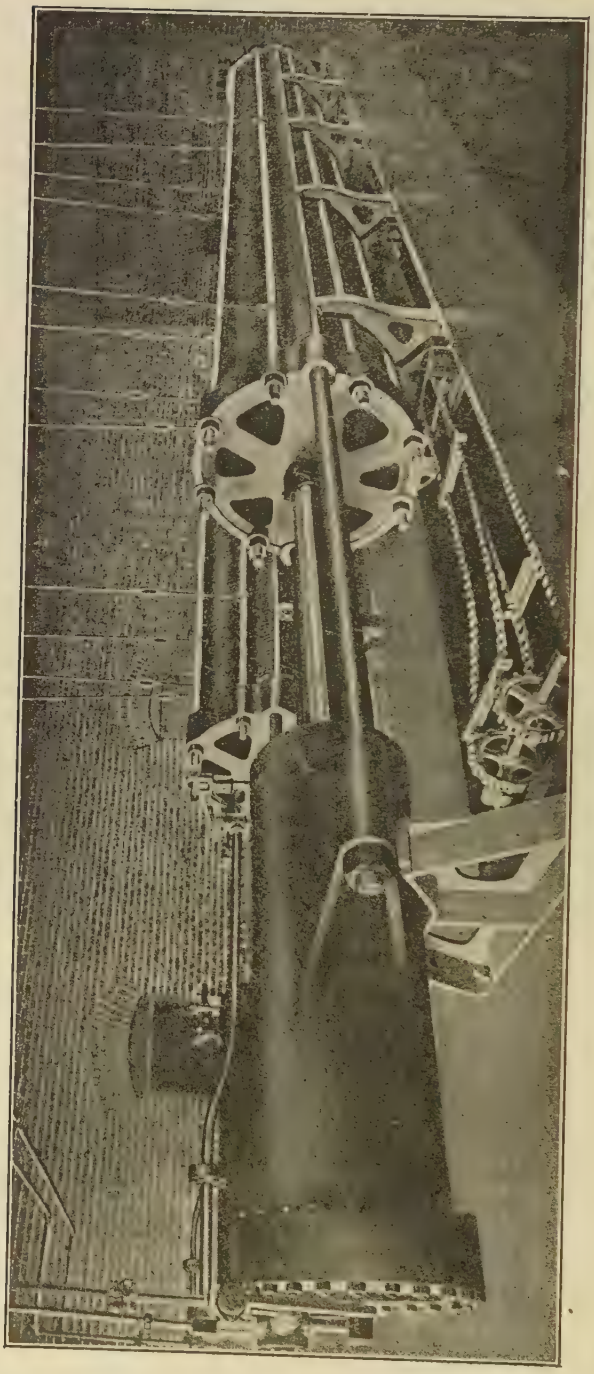


FIG. 257.

than when making low viscosity oils—as the viscosity increases with the boiling point in the same homologous series of hydrocarbons. The first fraction, separated at 36° Bé. (.8433 sp.gr.), is put into the low test burning oil fraction; the second fraction down to 32.5° Bé. (.8615 sp.gr.), being too high in specific gravity for burning oils, and having practically no value as lubricating oil, is separated for "fuel oil." The third fraction, cut at 28° Bé. (.886 sp.gr.), is used for making low viscosity lubricating oils, as described by chart, and the fourth for medium lubricating oils. The residue, which is heavy lubricating oil stock of dark color, is pumped out of the still through a coil of cast-iron pipe set in water called a cooler, in order to prevent oxidation when exposed to the air. The cool

Fig. 258.

oil is treated with from 20 to 50 lbs. of commercial 66° Bé.[1] sulphuric acid per barrel in an agitator of from 200 to 1000 barrels capacity in the same manner as described under burning oils, except that the agitation is kept on longer—one to two hours—and it takes longer for the sludge acid to settle—four to six hours. Fig. 258 shows the sludge being drawn from a 500 barrel agitator. The amount of acid used in treating depends on the color desired on the finished oil.

After drawing off the sludge, the oil is transferred to a "lye" agitator, where most of the remaining acid is washed out by agitation with water. It is then agitated with caustic soda of from 1 to 6° Bé. until a distinct alkaline reaction with phenolphthalein is obtained. The "lye" containing sulpho-compounds, formed by the acid treatment, is drawn off,

[1] Beaumé scale for liquids heavier than water.

and the oil washed well again with water, and finally with hot water, until a neutral reaction is obtained. The water is separated and the oil transferred to shallow tanks, where it is warmed to 150° to 160° F. by closed steam coils, and air blown up through it from a perforated coil until all the moisture is removed, leaving the oil clear and bright and ready for the market.

The "sludge" acid from the lubricating oils is black, asphaltic in nature, and very viscous, almost a solid mass. It, with the sludge from the burning oils, is agitated with water in a lead-lined separator; the weak acid recovered is concentrated in lead pans and finally in stills of cast iron to 66° Bé. and is then used over again. The residue is used for fuel, or worked into pitch.

Paraffin Wax. The slack wax expressed from the tar distillate usually contains from 30 to 40 per cent of oil, which is gotten rid of by one of the following methods: it may be mixed with naphtha and cooled until the wax crystallizes out, and then refilter pressed; or it may be removed by the process known as sweating. The "sweaters" consist of tiers of pans arranged in rooms, as shown in Fig. 259; the rooms are heated by steam coils, each room being known as an oven. The pans are first filled with water to the level of a wire screen at *A* and the melted wax is charged in until the pans are full, after which cold water is circulated through coil *B* until the wax solidifies. The water is then drawn off from underneath the solid cakes of wax by valve *C* and warm water circulated through coil *B* and the rooms also heated by steam coils. The heat causes the oil to sweat out of the wax, and it drains off and runs into a tank. The oil, or "foots," thus separated, containing some soft wax, is filter pressed and worked up the same as the unpressed tar distillate. The sweated wax remaining in the pans is melted, drawn off, and delivered to the filtering plant, where it passes through bone black or fuller's earth contained in long cylindrical tanks called filters in rooms heated from 130° to 180° F. This operation removes practically all of the color. It is then molded into cakes either in pans or between hollow plates cooled by the circulation of water in apparatus shown in Fig. 260, known as the "Gray Wax Caking Machine." [1]

The Steam Distillation. Spindle oils and cylinder stocks. In making special high-grade lubricating oils, the distillation of the crude oil is carried on in the same manner as the destructive distillation until just before the "cracking" point is reached, when steam is introduced as before mentioned; by this method decomposition is practically prevented. The yield of burning oil is therefore much lower and lubricating oil much higher. The distillation is carried on until about 15 to 18 per cent remains in the still. The reduced stock, known as steam refined cylinder stock, is pumped out through a cooler.

[1] Patented by A. McD. Gray (built by S. L. Moore & Sons of Elizabeth, N. J.).

The steam refined cylinder stocks are sometimes further refined by filtration through bone black or fuller's earth and are then known as filtered cylinder oils. Cylinder oils [1] are recognized by their high flash point and viscosity.

After the burning oil fraction has been separated, the rest of the distillate, passing over during the distillation, is called "spindle distillate." It contains considerable wax, which is removed by filter pressing in exactly the same manner as with the unpressed tar distillate. The pressed spindle distillate is reduced in the same manner as the paraffin oils, except that the reduced spindle oil stock, instead of being treated

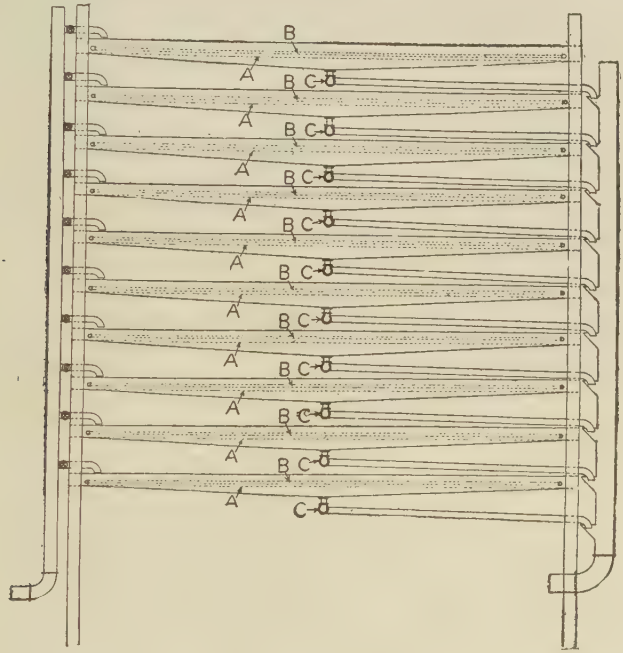


FIG. 259.

with acid is filtered through bone black, or fuller's earth, contained in cylindrical filters of about 15 to 20 tons capacity. The fuller's earth removes the asphaltic matter, and improves the color of the oil. The first oil running through the filter is almost colorless; but as the fuller's earth "adsorbs" the asphaltic matter, it soon loses in decolorizing value and the oil runs darker until it reaches a point where it is not practical to filter any longer, when the operation is stopped. The oil held by the fuller's earth is washed out by allowing naphtha to filter through it, and the naphtha remaining in the filter is collected by steaming it out with

[1] The problem of the lubrication of gas engine cylinders has created a new class of cylinder oils, which are made from the steam distillate (heavy distillate), from steam distillation and are of lower viscosity and fire test.

an open steam jet, and running it through a condenser, The oil washed out by the naphtha is separated by distillation, and the fuller's earth is heated in a retort nearly to redness in order to dry it and burn off the asphaltic matter, when it is used over again.

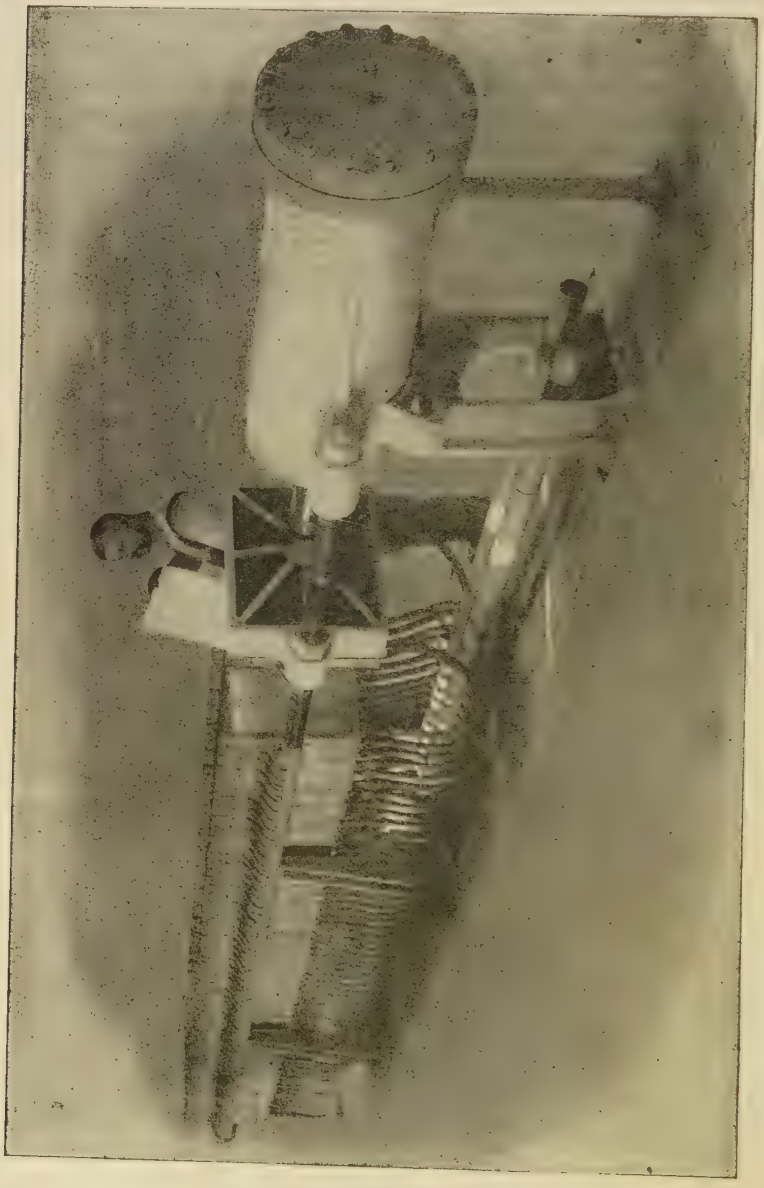


Fig. 260.—The Gray Wax Moulding Press.

Vaseline and "petrolatum" are reduced stocks made from selected crude oil by careful reduction and subsequent filtration through fuller's earth, or bone black.

Asphaltic Base Crude Petroleum. The refining of asphaltic base crude oil is substantially the same as described in the preceding methods, excepting the residue, which, instead of being tar, or cylinder stock, is asphalt. The burning oils are not of such good quality, a larger percentage of fuel oil is obtained, and the lubricating oils are of higher specific gravity and lower flash than those made from the paraffin base petroleum.

Natural Gas. Although natural gas always accompanies crude petroleum, it is often found independently. It consists principally of gaseous members of the paraffin series, of hydrocarbons, but contains small percentages of olefins,[1] nitrogen, carbon dioxide, and sometimes oxygen and hydrogen.

The increased consumption of gasoline has been of particular benefit to the natural gas producers, who have what is commonly called "Wet Gas." Wet gas being natural gas containing commercial quantities of very high gravity gasoline, which can be extracted by compression and condensation.

This gasoline is known as "Wild," "Casing Head" or "Natural Gas" gasoline, and is used to a large extent in blending with heavier products. From two to six gallons of this "Casing Head" gasoline can be separated from one thousand cubic feet of gas under compression of two hundred and fifty pounds.

Natural gas is used principally for illuminating and fuel purposes, also to some extent in the manufacture of lampblack.

Shale Oil. In Scotland, and to a small extent in other countries, paraffin oils are obtained by the destructive distillation of bituminous shale. The formation of the oil is dependent on the decomposition of the organic matter present.

Shale varies in color from dark gray to almost black, the products obtained being ammonia water (separated as a sulphate), paraffin wax, paraffin oils, burning oils, and phenols. The shale is first reduced to very small pieces, and then distilled continuously in circular vertical retorts, by charging in the top through a hopper, and drawing the exhausted shale out at the bottom. Steam is usually introduced into the retort. The vapors pass through a condenser, and the crude shale oil and ammonia liquor are separated. The remaining gases are subjected to a scrubbing process which consists of passing the gas through coke towers, where it comes in contact with streams of oil and water; the oil absorbs a large portion of the hydrocarbons, and the water takes up the ammonia, the residual gas being used for fuel. The compression process has also been used for condensing the gases; by this process the gas is subjected to low temperatures, and under a pressure of from 75 to 150 lbs. per square inch, but this method is said to be more expensive than the process of scrubbing. The crude shale oil [2] is dark in color, ranging

[1] University Geol. Survey of Kansas, Vol. IX.
[2] Redwood, "Petroleum and its Products."

in specific gravity from .86 to .89, and having a cold test of 90° F. due to solid paraffins. It is distilled by either the intermittent or continuous process to coke in practically the same manner as with the tar from crude petroleum, except that steam is introduced through perforated coils during the distillation process. The treatment of the various fractions i.e., naphtha, burning oil, paraffin distillate (containing the paraffin wax)—consists of a treatment with sulphuric acid and alkali in the same manner as with petroleum; the alkali in this case, in addition to neutralizing the acid, removes the phenols which have been formed during the first distillation. The phenols are liberated[1] from the waste "lye" by passing carbon dioxide through it.

Ozokerite. Ozokerite, or earth wax, is, as the name implies, a wax-like substance found in small quantities throughout the world, usually associated with rock salt or gypsum. The principal deposit occurs in the neighborhood of Boryslaw, in Galicia. It consists largely of solid paraffin hydrocarbons, and is supposed to have resulted from the evaporation and decomposition of crude petroleum. Like petroleum, it is found in different ages, but principally in the Tertiary and the Cretaceous. The appearance and physical character vary, some grades being soft and others brittle, and the color ranges from yellow to black. The specific gravity averages from .85 to .89 and the melting point[2] from 130° to 156° C. The Galician ozokerite is mined by sinking a shaft and then following the vein. Thus mined, it often contains much earthy matter. The purest pieces are first separated by hand picking, and the remainder is dumped into tanks of cold water; the purer ozokerite rises to the surface and is skimmed off, and the earthy matter, containing some ozokerite, sinks to the bottom. This residue is then heated in boiling water, when practically all of the ozokerite rises to the surface and is separated. The earth is finally extracted with naphtha, thereby dissolving the last traces of ozokerite. Ceresin, or refined ozokerite, is used largely as a substitute for beeswax, and is prepared by treating with sulphuric acid, washing with water, and neutralizing with caustic soda, as described under petroleum refining, and subsequent filtration through bone-black or fuller's earth. It varies in color from white to yellow, according to the degree of refining. Ozokerite is sometimes distilled and worked up for paraffin wax.

Asphalt. The name asphalt is generally applied to that class of bitumens found naturally in the earth in various parts of the world. It consists principally of compounds of carbon and hydrogen, also compounds containing nitrogen, oxygen, and sulphur and some mineral matter, and is considered to have resulted from crude petroleum. Asphalt is black in color, and melts easily on the application of heat. It is partly soluble in petroleum spirit and completely soluble in carbon disulphide,

[1] "Mineral Oils and their By-products," I. I. Redwood.
[2] Redwood, "Petroleum and its Products."

the part soluble in petroleum spirit being designated "petrolene," and the part soluble in carbon disulphide, "asphaltene." The principal uses are for street paving, weather-proofing, paints and japans. The most important production is from "Pitch Lake," on the island of Trinidad, which is 135[1] feet deep at the center and originally covered an area of approximately 127 acres, and is estimated to contain several million tons of asphalt.

The crude lake asphalt, according to Clifford Richardson,[2] contains the following constituents:

Water and gas	29.0%
Organic matter not bitumen	7.0
Mineral matter	25.0
Bitumen	39.0
	100.0%

The method of refining consists of melting and removing the mineral matter which subsides. The composition of the refined Trinidad Lake Asphalt is given as follows:

Bitumen (soluble in carbon disulphide)	56.4%
Organic matter, not bitumen	6.7
Mineral matter	36.9
	100.0%

The asphalt residues from crude petroleum so closely resemble the natural asphalts that they cannot be distinguished with certainty. Petroleum asphalts are used principally for weather-proofing.

Other deposits occur in California, Utah, Mexico, Venezuela, Cuba, France, Switzerland, and Germany.

Method of Testing

Crude Petroleum. The New York Produce Exchange defines crude petroleum as follows: "Crude petroleum shall be understood to be a pure natural oil, neither steamed nor treated, free from water, sediment, or other adulteration, of the gravity of 43° to 48° Bé." Since the production of the lower Baumé gravity oils, the limitations in regard to gravity have been relaxed.

In order to ascertain whether or not the petroleum conforms to the above rule, it is distilled in 10 per cent fractions, and the Baumé gravity determined on each fraction. It is obvious that, from the complexity of crude petroleum, each succeeding fraction would show a somewhat regular

[1] Report of the Inspector of Asphalt and Cements. Eng. Dept. District of Columbia. 1892.

[2] "The Modern Asphalt Pavement," C. Richardson.

gradation in specific gravity, whereas, in cases of adulteration, it would be more or less irregular.

In order to ascertain the commercial value of crude petroleum, Dr. Engler recommends the distillation of 100 c.c. from a distillation flask of the dimensions in cubic centimeters shown in Fig. 261. The distillation is controlled so that from 2 to 2½ c.c. of distillate pass over per minute, heat being applied by means of a Bunsen burner. At the beginning of the distillation a piece of wire gauze is interposed between the flame and the flask, but finally the naked flame is used. As soon as the temperature reaches 150° C., the burner is removed until the temperature falls 20°. It is then reheated to 150° C., and the cooling and heating process continued until no more distillate passes over. This fraction is classed as naphtha. The distillation is then continued until 300° C.[1] is reached, when the temperature is allowed to drop as before. This fraction is separated as illuminating oil, the residue representing the lubricating oil.

In Dr. Ubbelohde's modification of the Engler method, the condenser tube is bent vertical at the end farthest from the flask in order to drop the distillate into one or another of a series of graduated test tubes contained in a holder. The temperature at which the first drop of distillate runs into the test tube is taken as the beginning of boiling. The distillation is then continued at two drops

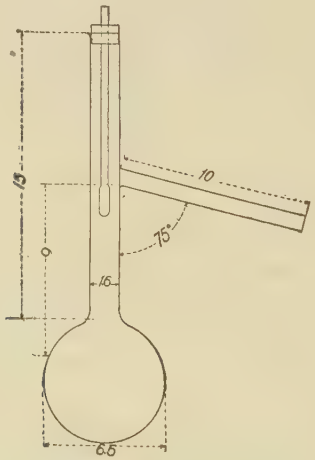


Fig. 261.

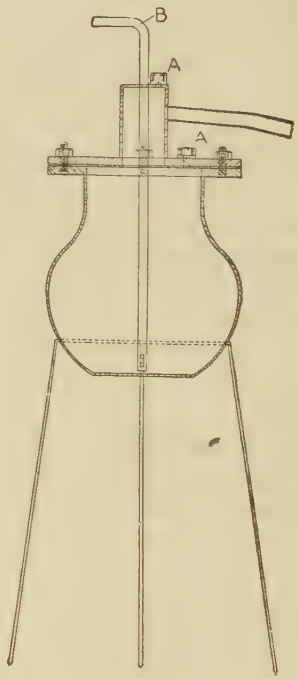


Fig. 262.

per second up to 300° C., the fraction up to 150° C. being taken as naphtha, and from 150 to 300° C. as burning oil.

[1] When distilling petroleum made up largely of the naphthene hydrocarbons, the burning oil is separated at 285° C. instead of 300° C.

In order to determine roughly the yield of products likely to be obtained in actual refining, the author recommends the distillation of from two to four liters of the crude oil. A convenient form of still is shown in Fig. 262. The distillation is carried to coke and controlled so that from 5 to 10 c.c. of distillate pass over per minute, it being separated in one per cent fractions, and the Baumé gravity determined on each fraction. All of the fractions over 58° Bé. are added together for the naphtha fraction, those between 58° and 36° Bé. for the burning oils, and the distillate passing over, below 36° as lubricating distillate, the residue being coke.

Sulphur. Since the illuminating oils made from crude petroleum of high sulphur content require special treatment, it is desirable, in estimating the value of crude petroleum, to know the percentage of sulphur it carries. The method of Mr. C. I. Robinson is the quickest and simplest method known to the writer. This method does not give absolutely accurate results, but is on account of its quickness of great service to the refiner. For more accurate results see method of Allen, Bureau of Mines, Tech. Paper 25. It is described[1] as follows: "(1) A dilute aqueous solution of tropæolin, 00. (2) A solution of sulphuric acid, 1 c.c. equal to 0.001 grams of sulphur. (3) A solution of sodium carbonate equivalent to the sulphuric acid. About 5 or 6 c.c. of the oil to be examined are poured into the Erlenmeyer flask *A*, Fig. 263, which is about 15 or 20 c.c. capacity, and contains a wick passed through a glass tube which is held in place by a cork. The flask with the wick is then weighed, the second decimal place being sufficiently accurate. It is then placed under the small tube *C*, which is connected with the absorption apparatus *D*, one limb of which contains glass beads,[2] and into which 5 c.c. of the standard alkali solution has been run. *D* is connected with suction. When the apparatus is all in place, the suction is turned on, and the wick *B* is lighted. The suction draws all the products of combustion through *D*. The *S* contained in the oil is all burned to SO_2 and SO_3, and is absorbed by the sodium carbonate solution. The oil is allowed to burn about thirty minutes—until 2 or 3 grams are consumed. The tube *C* is rinsed into *D*, a few drops of tropæolin added, and the excess of sodium carbonate titrated with the standard sulphuric acid, and the amount of sulphur calculated."

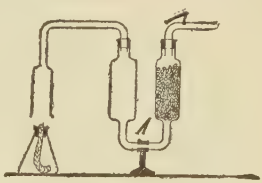


Fig. 263.

Specific Gravity. The Baumé hydrometer is in general commercial use in this country for determining the "gravity;" but, in cases where extreme accuracy is required, the pynknometer should be used. The

[1] The rapid method for the estimation of sulphur in crude petroleum and illuminating oils, Proc. Va. Chemists Club, Vol. I, p. 53, 1908. C. A., Vol. III, p. 115, and Vol. III, p. 2627.

[2] Mr. Robinson advises using broken glass rods instead of beads, the latter being usually made of soft glass so soluble in water as to increase the alkalinity of the solution to the extent of rendering the determination worthless.

Westphal balance is sometimes found convenient to use instead of the hydrometer.

Water and B. S. are determined by mixing the crude petroleum with naphtha, half and half, in a 100 c.c. cylinder tapered at the bottom and graduated in tenths, and allowing the mixture to stand for twenty-four hours. The water and B. S. settle to the bottom, and are reported collectively. A centrifuge is sometimes used for forcing the separation.

Illuminating Oils. The specific gravity and sulphur are determined as in the case of crude oils.

Color. Redwood recommends the use of Stammer's chromometer, which consists of two cylinders closed at the ends with glass. By means of a mirror, light is reflected upward through the cylinders, and the optical arrangement at the top contains prisms allowing both columns to be observed through one eye piece on a circular field divided in the center. The graduated cylinder is filled with oil to be tested, and a glass disk of standard color interposed between the mirror and the eye piece of the other cylinder. The wheel lowers the small cylinders until the divisions on the field of the eye piece are of the same color. The color of the different grades of burning oils on the market are as follows:

Water white		
Standard white	40	Stammer's chromometer
Prime white	50	"
Superfine white	190	"

Flashing Point and Fire Test. The instruments used for these tests are of two types—viz., the open and closed cups. The Tagliabue and Saybolt open cups and the Abel closed cup are among those generally used. The Tagliabue cup consists of a glass cup supported in a copper bath, and heated by a spirit lamp. The cup is filled with the oil to be tested, a thermometer placed in it so that the bulb is covered, and the oil heated slowly, the flashing point being determined by passing a small flame over the surface of the oil until the vapor given off flashes momentarily. The heating is then continued until the oil ignites and burns, which temperature is taken as the fire test.

The Saybolt electric tester, which has been adopted by the New York Produce Exchange, is of similar construction, but the flash is tested by passing a spark from an induction coil between two platinum wires placed over the oil. The water is heated to 100° F., then the flame removed and the cup filled with oil and placed in the bath. A spark is passed for every rise of one degree, and when the oil has reached 90° F. it is necessary to heat again. After the oil has flashed, the sparks are passed at temperatures as follows: " In 110 (fire test) and upwards the flashing point after the first flash (which generally occur between 90° and 95°) shall be taken at 95°, 100°, 104°, 108°, 110°, 112°, 115°. In a 120°

and upwards, after the first flash, 100°, 105°, 110°, 115°, 118°, 122°, 125°. In a 130° and upwards every 5° until the burning point is reached."

The open test method is affected by drafts, and is variable. For this reason the closed test cup was introduced.

The Abel apparatus, adopted by England, is described in the petroleum act of August 11th, 1879, as follows: "The oil cup consists of a cylindrical vessel 2 ins. in diameter, 2.2 ins. in height, (internal), with outward projecting rim 0.5 in. wide, $\frac{3}{8}$ in. from the top, and $1\frac{7}{8}$ ins. from the bottom of the cup. It is made of gunmetal or brass 17 B.W.G., tinned inside. A bracket, consisting of a short, stout piece of wire bent upwards and terminating in a point, is fixed to the inside of the cup to serve as a gauge. The distance of the point from the bottom of the cup is $1\frac{1}{2}$ ins. The cup is provided with a close-fitting, overlapping cover, made of brass (22 B.W.G.), which carries a thermometer and test lamp. The latter is suspended from two supports by means of trunnions, upon which it may be made to oscillate; it is provided with a spout, the mouth of which is $\frac{1}{16}$ in. diameter. The socket which is to hold the thermometer is fixed at such an angle, and its length is so adjusted, that the bulb of the thermometer, when inserted to its full depth, shall be $1\frac{1}{4}$ ins. below the center of the lid."

"The cover is provided with three square holes, one in the center, 0.5 ins. by 0.4 ins., two smaller ones, 0.3 ins. by 0.2 ins., closed to the sides and opposite to each other. These holes may be closed and uncovered by means of a slide moving in grooves and having perforations corresponding to those on the lid. In moving the slide so as to uncover the holes, the oscillating lamp is caught by a pin fixed in the slide and tilted in such a way as to bring the end of the spout just below the surface of the lid. Upon the slide being pushed back so as to cover the holes, the lamp returns to its original position. Upon the cover, in front of and in line with the mouth of the lamp, is fixed a white bead, the dimensions of which represent the size of the test flame to be used."

"The heating vessel or water bath is filled by pouring water into the funnel until it begins to flow out of the spout of the vessel. The temperature of the water at the commencement of the test is to be 130° F. The bath, having been raised to the proper temperature, the oil to be tested is introduced into the petroleum cup, being poured slowly until the level of the liquid just reaches the point of the gauge fixed in the cup. The results obtained with this cup show on the average about 27° F. lower than the open cup. Details of the operation of the instrument are given by Redwood in "Petroleum and its Products," Vol. II.

Lamp Tests. The usual practice is to burn samples of the oil in lamps of ordinary construction for from five to twenty-four hours, observing the diminution of the flame and the incrustation of the wick.

Lubricating Oils. In this country the fire test is generally determined by means of the Cleveland cup. The method is substantially the same as

with the burning oils, with the exception that the oil is heated at the rate of 10° per minute, and the flashing point tested with a small bead flame for every rise of 5°. The fire test is, as a rule, from 60 to 80° higher than the flash point. As the open cup tests are easily affected by drafts, they are subject to errors of 5°.

Closed Test. The Pensky-Martin cup is generally used for this test. It is similar in construction to the Abel cup, and contains a stirring apparatus by means of which a uniform temperature of the oil may be obtained. The results obtained by this instrument are, as a rule, close to those obtained by the open cup, but are not subject to errors of the open cup.

Cold Test (Setting Point). As the solid paraffins are poor lubricants, oils of low cold test are desirable. The method commonly used may be described briefly as follows: In an ordinary 4-oz. sample bottle, about one-third full of the oil to be tested, the bulb of a thermometer, which passes through a cork in the neck of the bottle, is just immersed in the oil. The sample is cooled slowly to 50° F. and then subjected to a freezing mixture of ice and salt. The bottle is removed for every few degrees drop in temperature and tilted to see if the oil is still liquid, the temperature at which it just ceases to flow being taken as the cold test or setting point. If the conditions of this method are carefully followed, the results should check within 1° or 2°. In the case of reduced stocks which have not been treated either by acid or filtration through fuller's earth or boneblack, the cold test is unreliable, as the tarry matter present in these oils seems to hold the wax in solution. For illustration, some reduced stocks which show a cold test of 30° F. before filtration through fuller's earth or boneblack are solid at ordinary temperature after filtration. In the case of oils having cold tests higher than 45° F. it is customary to reverse the process—that is, freezing the sample solid, first, to about 20° F. lower than the point at which it congeals, and then gradually warming in water until on tilting it shows a perceptible flow.

Color. The color determination of lubricating oils is not only important as a matter of convenience in keeping records, but indicates the degree of refining the oil has received. For this purpose the Lovibond tintometer is to be recommended. This instrument is made of wood and divided longitudinally by a partition, one side to be used for the sample and the other side, which is slotted, for the standardized colored glasses. The oil, depending upon the depth of color, is tested in cells from $\frac{1}{2}$ in. to 12 ins. long. Very dark red oils, for instance, are tested in $\frac{1}{2}$ in. cells, the lighter color red oils in 2 ins., and pale oils in 6 ins. or even 12 ins. cells. The cell, filled with oil, is placed on one side of the partition, and the standard glasses in the slot of the other side until the color is matched.

Odor. The odor of lubricating oils should be what is known in the trade as "sweet."

Viscosity. The viscosity or internal friction, sometimes expressed as the "body" or "fluidity," although an arbitrary test, is an important

one in selecting a satisfactory lubricant. The instruments principally used for making this test are of the same general type, and are known as efflux viscosimeters, the main difference between the instruments being in the dimensions of the capillary through which the oil runs and the amount of oil used for the test. Oils of low viscosity, as, for example, those of the engine, machine, and spindle oil classes, are usually tested at temperatures ranging from 60° to 100° F., and cylinder and other high viscosity oils at 210° to 212° F. The principal instruments of this type are the Engler, Redwood, Saybolt, Tagliabue, and Universal.

The Engler viscosimeter, used in Germany and also to a considerable extent in this and other countries, consists of a reservoir *A*, for the oil, enclosed by cover *A*, set in bath *B*. The capillary tube *a* is stopped by plug *b*; 240 c.c. of the oil to be tested are poured into the reservoir, and should be just on a level with the points of the studs *cc*. The time required for the delivery of 200 c.c. of distilled water at 20° C. from a charge of 240 c.c. should be from 51 to 53 seconds. The temperature is regulated by means of a ring burner placed under the oil bath. When the proper temperature has been attained, the plug is withdrawn and the outflow of 200 c.c. timed by a stop watch. The time in seconds required for the oil, divided by the time in seconds for water at 200° C., is taken as the "specific viscosity."

The results obtained by the Redwood [1] instrument are compared with rape oil as follows: The time in seconds required for the outflow of 50 c.c. of the oil at 60° F. is multiplied by 100 and divided by 535, which is the average number of seconds required for rape oil under the same conditions. The result is multiplied by the specific gravity of the oil and divided by 0.915, the specific gravity of rape oil.

The Tagliabue, Saybolt and Universal instruments are arbitrary, the results being expressed in seconds for the efflux of about 60 c.c. of the oil.

Paraffin Wax. *Melting Point.* The "English test," which is in reality the solidifying point, is determined by stirring the melted wax in a small cup about $2\frac{1}{2}$ ins. in diameter by about 2 ins. deep until the latent heat given up by the crystallization of the wax arrests the fall of the mercury column momentarily. The "American test" gives results about 3° F. higher than the English test, and is determined as follows: A hemispherical cup $3\frac{3}{4}$ ins. in diameter is three-quarters filled with melted wax, which is allowed to cool without stirring until a thin film forms on the top, and extends from the sides to a thermometer with a round bulb $\frac{1}{2}$ in. in diameter, suspended so that it is three-quarters immersed in the center of the cup. As the American method is slow, it is customary to take the English test and add 3° F. for the American.

Color. This is determined by the Lovibond instrument, using cells from 6 ins. to 24 ins. in length, the wax being melted. As with the oils, it shows the degree of refining.

[1] Described in "Petroleum and its Products."

Odor and Taste. The odor and taste must be absolutely sweet in the case of refined wax, but the semi-refined waxes usually have a slight odor and taste of light oil.

Per Cent of Oil. The determination of oil in scale and slack wax is determined by pressing a 500-grain sample, at a temperature of 60° F., between pieces of muslin cut to fit the test cup. The oil is absorbed by pieces of blotting paper placed above and below the cloth containing the wax in the test cup.

The cup and plunger are cooled to 60° F. before putting in the sample of wax, which has also been cooled to 60° F. The lever press, Fig. 264, built by the S. L. Moore & Sons Corp. of Elizabeth, N. J., is the one in general use in this country. The test cup and plunger are $5\frac{5}{8}$ ins. in diameter, and a pressure of nine tons on the total surface is applied for five minutes.

Asphalt. *Melting Point.* A number of methods are in use for the determination of the so-called "melting point." Products of this class, however, on account of their complex nature, do not have a true melting point. The methods in general use are as follows:

Ball and Ring Method. "A $\frac{1}{4}$ in. deep by $\frac{5}{8}$ in. diameter ring should be level full of solid asphalt, with some adhering to the top and bottom. This can be done best by filling the ring rounding full with asphalt, cooling in cold water for a few minutes, and then cutting off the excess with a hot knife. There must be no air bubbles inside the ring. A $\frac{3}{8}$-in. steel bicycle ball, weighing about 5 grams, is then placed in the center of the asphalt and the ring hung on a level with the mercury bulb of a thermometer, the point immersed in a beaker of water. For asphalts melting below 100° F. the water should be about 40° F. at the start; for asphalts melting below 150° F., 60–70° F.; for asphalt melting above 150° F., not more than 80° F. The water and beaker should be heated 10° F. per minute, and should not vary more than 1° F. The melting point is the temperature where the ball and pitch begin to drop rapidly on leaving the ring, which is usually about $\frac{1}{2}$ in. below the bottom of the ring.

Fig. 264.

The Kraemer and Sarnow method[1] is similar to the ball and ring method, except that the asphalt is contained in a 6–7 m.m. open glass tube, and 5 grams of mercury placed on the top, the tube being suspended in water near the bulb of a thermometer. The water is heated until the mercury drops through with the asphalt.

[1] Chem. Ind. 1903, 26, (3), 55–57.

A recent electrical method[1] has been devised by Mr. Herbert Abraham, in which the temperature is raised by a coil of resistance wire placed in the bath. The coil is connected with a rheostat, by means of which the temperature can be easily regulated. The particular advantage of this method is the uniform rate at which the asphalt can be heated.

Penetration: (Consistency or hardness). The instruments generally used are the Bowen, the Dow, and the New Yorking Testing Laboratory Penetrometers, all of which are described by Mr. Clifford Richardson in the "Modern Asphalt Pavement." A sample of the asphalt is subjected to the impression of a weighted standard needle for a specified time, at a definite temperature, the penetration of the needle being recorded on a dial.

Mr. Herbert Abraham, in the Proceedings of the American Society for Testing Materials, Vol. IX, 1909, describes his consistometer, which is said to give a more accurate measurement of the true hardness of asphalt than the penetrometers.

Petrolene and Asphaltene. The bitumen soluble in petroleum spirit has been designated arbitrarily "petrolene," and the part soluble in carbon-disulphide as "asphaltene." Some users of asphalt vary their specifications for petrolene and asphaltene, basing their proportions on what in practical work seems to give the best results. The petrolene is first determined by extracting a sample with petroleum spirit, the amount dissolved representing the petrolene; the residue is then extracted with carbon-disulphide, the part dissolved representing the asphaltene.

Cracking Processes.[2] The process of "cracking" petroleum consists in the decomposition of hydrocarbons by exposing them to temperatures above their normal boiling-points, producing thereby hydrocarbons of lower and higher boiling-points than were contained in the original mixture so treated. All "cracking" processes may be divided into four general groups, viz.:

1. Those in which the hydrocarbon mixture in liquid form is subjected to highly heated surfaces.

2. Those in which the vaporized hydrocarbon mixture is subjected to high temperatures.

3. Those in which the hydrocarbon mixture in vapor form is subjected to high temperatures in the presence of a catalyst.

4. Those in which the hydrocarbons are distilled under pressure.

The products obtained by the cracking process are: fixed gas, gasoline, kerosene, and aromatic hydrocarbons (benzene and toluene). While most processes have been devised for the manufacture of gasoline, the European War has caused a good deal of attention to be directed to these processes for the production of toluene for the manufacture of trintrotoluol, which is used extensively in explosives.

[1] Described by Mr. Herbert Abraham in Proceedings of American Society for Testing Materials, Vol. IX, 1909.

[2] T. T. Gray and Frederick C. Ring.

Speaking generally it may be said that high temperatures are necessary for cracking hydrocarbons, and that the higher the temperatures the greater is the volume of fixed gas formed. Pressure is used to bring about the cracking at lower temperatures, in order to avoid this otherwise large gas loss.

Catalytic agents such as finely divided metals are sometimes used to accelerate the decomposition or cracking process, but there are many processes claiming catalytic action, where the only function of the so-called "catalysts" used is one of increased heating surface.

Dalton [1] in 1809, made the first scientific investigation of the decomposition of hydrocarbons by submitting methane and ethylene to the action of electric sparks.

Faraday,[2] in 1825, discovered benzene and unsaturated hydrocarbons in products obtained by subjecting oil to high temperatures.

That oils will decompose under conditions of superheat and pressure has been known since the early days of petroleum development, having been observed by Silliman in 1855 prior to the drilling of the first oil well. Leet describes the cracking process as first conducted on a commercial scale under ordinary atmospheric pressure.

Young,[3] in 1865, patented his "Improvements in treating hydrocarbon oils," which was taken out for cracking shale oils under a pressure of 20 pounds.

Berthelot,[4] in 1866, published his classical researches showing the effect of heat on various hydrocarbons. Acetylene, heated to the temperature at which glass softens and which he assumed to be 600° to 700° C., formed liquid hydrocarbons, and, heated in the presence of coke, decomposed to carbon and hydrogen. In a later series of experiments in which various hydrocarbons were passed through a red-hot porcelain tube, he found benzene gave diphenyl, chrysene, and a resinous body; toluene gave benzene, toluene, naphthalene, a crystalline product volatile at 270° C., a liquid hydrocarbon named by him benzyle, and anthracene; styrolene gave benzene and acetylene; styrolene and hydrogen gave benzene and ethylene; styrolene and ethylene gave naphthalene principally but some benzene; styrolene and benzene gave anthracene, naphthalene, and diphenyl; benzene and naphthalene gave anthracene; diphenyl gave benzene and chrysene; xylene gave toluene principally, also xylene, benzene, naphthalene, and anthracene; cumolene gave toluene and xylene for the main part with smaller quantities of benzene, also cumolene, naphthalene, anthracene, chrysene, and benzerythrene.

Thorp and Young [5] in 1871 distilled paraffin wax of 44.5° C. melting-

[1] Phil. Trans. 99 (1809), 446.

[2] Ibid., 440 (1825).

[3] Eng. Pat. 3345 (1865).

[4] Ibid. 63 (1866), 788,834; Compt. Rend., 62 (1866), 905, 947; Bull. Soc. Chim. Paris, 2, 7 (1867), 217.

[5] Proc. Roy. Soc. 19 (1871), 370; 20 (1872), 488; 21 (1873), 184.

point under pressure, obtaining almost a complete conversion of same into liquid hydrocarbons. On examination of the fraction distilling below 100° C. (212° F.), it was found to consist mainly of olefins. The fraction below 200° C. was made up of olefins and paraffins, but no benzene hydrocarbons were found.

Abel,[1] in 1877, took out a patent in which petroleum is treated with anhydrous aluminium chloride or other metallic chloride at 100° C. to 600° C. with the production of light oils.

Benton,[2] in 1886, patented his "Improvements in the methods and means of refining crude and refuse petroleum oil and the like." This process consisted in pumping the oil to be cracked under a pressure of 500 pounds or more to the square inch, and a temperature between 700° and 1000° F., through a coil of pipe heated in a furnace, and expanding the

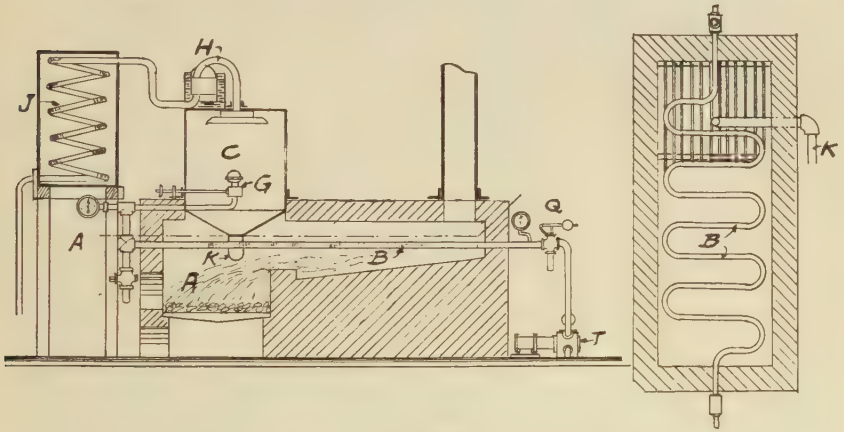


Fig. 265.

vapor into a chamber connected with a condenser. This apparatus, Fig. 265, was designed to produce kerosene from heavier and less valuable oils. It consists of a series of pipes B, heated by means of a furnace A, and communicating on one side with a force pump T, and on the other side with a vapor chamber C, which may be heated or partially exhausted. The pressure is regulated by a valve G, a safety valve Q, being also provided. The unvolatilized liquid passes from the chamber C at K, and the vapor passes through the primary condenser H to water cooled condenser J.

Krey,[3] in the same year, took out a patent in which he used pressure of from 2 to 4 atmospheres.

Dewar and Redwood,[4] in 1889, developed a very interesting process for

[1] Eng. Pat. 4769 (1877).

[2] Eng. Pat. 1922 (1887); U. S. Pats., 342,564, 342,565 (1886).

[3] Ger. Pat. 37,728 (1886).

[4] U. S. Pats. 419,931, 426,173 (1890); Eng. Pats. 10,277 (1889), 13,016 (1890); 5971 (1891); Ger. Pat. 53,552 (1889).

distilling oil under pressure to increase the yield of illuminating oil. In their apparatus there is free communication between the still and the condenser, and the cracked products are condensed under pressure, see Fig. 266.

The still is charged about half full through charging line *E*, and all other space not occupied by the oil is charged with carbonic or other fixed gas

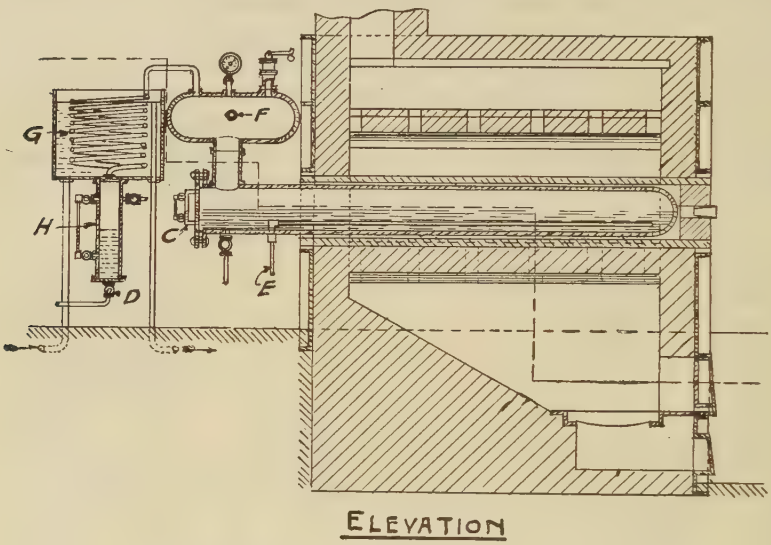


Fig. 266.

through gas line *F*. The pressure is maintained by closing control valve *D* on the condenser outlet line. The vapor is condensed in the condenser coil *G*, the condensate passing to a receiving tank *H*, which may be emptied at intervals.

The cover *C* is removed occasionally to clean out the residue.

The foregoing methods were all designed to increase the yield of illuminating oils from less valuable distillates. In the operation of these processes, the production of kerosene would be accompanied by a production of gasoline, but up to that time, 1890, there was practically no demand for gasoline, and the manufacturers left in the kerosene what is now known as the

gasoline fraction, and the finished kerosene oil had to stand specified flash tests. The internal combustion engine has reversed this condition, so that to-day gasoline has specified boiling-point limits to prevent its adulteration with kerosene.

Laing,[1] in 1892, took out a patent for cracking mineral oils under atmospheric pressure. In his apparatus, Fig. 267, oil is pumped continuously into the first compartment B_1; the vapors thus pass L_1 to the condensing coil M_1 and fall into compartment B_2. This same process is repeated through compartment B_3 and B_4.

The vapors pass from compartment B_4 through vapor pipe N to a condenser coil. The residue flows continuously through outlet T and cooler

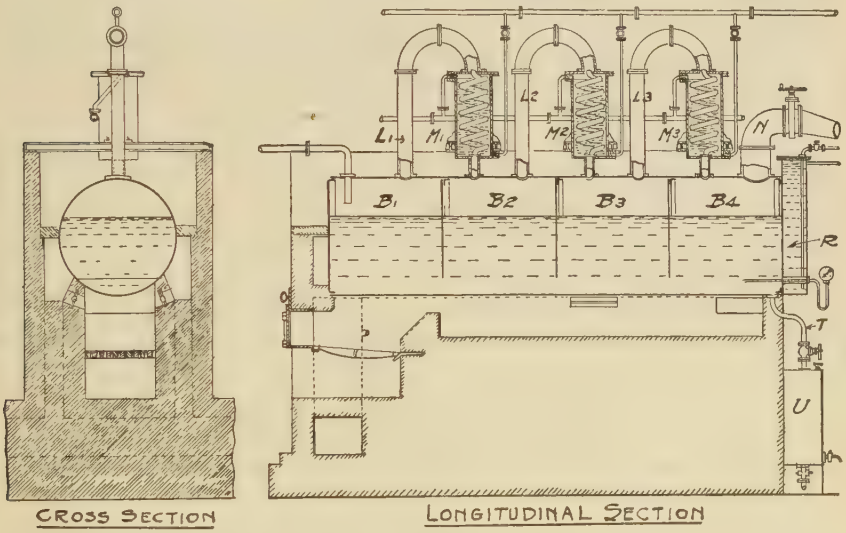


FIG. 267.

U to the receiving tank and is said to have the consistency of pitch when cold. R is a water jacket to prevent overheating of the end compartment B_4.

This process is more a continuous distillation process than a cracking process.

Cowper-Coles,[2] in 1906, passed paraffin oil vapors through small tubes heated to 1700° F. (926° C.), in order to decompose them for the production of motor fuel.

In 1906, Day [3] patented a process for distilling petroleum under pressure in the presence of hydrogen and a catalyst, mentioning palladium black or spongy platinum as suitable catalytic agents. Sabatier[4] in 1908,

[1] U. S. Pat. 488,767 (1892).
[2] Eng. Pat. 27,945 (1906).
[3] U. S. Pat. 826,089 (1906).
[4] Fr. Pat. 400,141 (1908).

patented a catalytic cracking and hydrogenation process, in which the heavy oil vapors first decomposed by passing them over finely divided metals at 400° C. were then combined with hydrogen and again passed over finely divided metals at a temperature of 150°–300 C.

In 1908 Noad and Townsend [1] passed oil mixed with water over highly heated scrap iron.

Testelin & Renard, [2] in 1908, obtained a patent for spraying petroleum into a coil by means of steam, heating to 400–450° C. under a pressure of 5 atmospheres, and then passing through a coil filled with burnt clay.

In 1909 Wassmer [3] used electrically heated conductors to crack petroleum vapors; and in 1910 Adams[4] proposed an incandescent electric heater.

Burke,[5] in 1911, decomposed oil at low pressure and condensed the cracked vapors at high pressure.

In 1912, Leffer [6] distilled petroleum in the presence of an inert gas under a pressure of 10 to 11 atmospheres and a temperature of 410° C.

Lamplough,[7] in 1912, decomposed oil in the presence of steam and nickel in a retort at dull red heat under pressure, using 20 to 60 parts of water to 100 parts of oil.

Ellis [8] in 1912, injected heavy oils with a small amount of air through nozzles into a retort charged with fire-brick, or other refractory material, under a pressure of 30 to 50 pounds.

Turner,[9] in 1912, passed water and oil through a coil heated at 400–800° F. and 60 pounds pressure where vaporization took place; he then passed the vapor through another coil heated to 1000–1400° F. and condensed it under atmospheric pressure.

In 1913 Renard[10] patented a process for converting petroleum into low boiling-point products by decomposing, under pressure, and distilling at atmospheric pressure.

G. W. Gray,[11] in 1913, cracked oils by heating them in the presence of anhydrous aluminium chloride, ferric or other metallic chlorides, at a temperature below the final boiling-point of the product desired.

In 1913 Moeller and Wolterick[12] developed a cracking process in which

[1] Eng. Pat. 13,675 (1908).

[2] Eng. Pat. 16,881 (1908); U. S. Pat. 1,138,260 (1915); Fr. Pats. 393,554 (1908), 416,244 (1910); Ger. Pats. 268,176 (1908), 226,958 (1909).

[3] Eng. Pat. 26,936 (1909).

[4] U. S. Pat. 976,975 (1910).

[5] Eng. Pat. 16,931 (1911); Fr. Pat. 432,762 (1911).

[6] Eng. Pats. 2329 (1912); 19,051 (1912); 4140 (1913); Fr. Pat. 454,580 (1913).

[7] Eng. Pats. 19,702, 28,101 (1912); Fr. Pat. 457,877 (1913); Int. Conv. Aug. 28 and Dec. 15, 1912.

[8] Eng. Pat. 25,631 (1912); Int. Conv. Apr. 1, 1912.

[9] U. S. Pats. 1,046,683 (1912); 1,151,422 (1915); Eng. Pat. 25,832 (1912); Fr. Pat. 451,162 (1912).

[10] Eng. Pat. 3413 (1913); Fr. Pat. 462,286 (1913).

[11] Eng. Pat. 17,838–9 (1913); U. S. Pat. 1,193,540–1 (1916); Int. Conv. June 23, 1913.

[12] Eng. Pat. 1611 (1913).

oil vapors mixed with steam superheated to 700–800° C. were passed over coke heated to 600–800° C.

Snelling,[1] in 1913, proposed to heat low-grade crude oil and heavy oils in a still one-eighth to one-half full until a pressure of 600 to 800 pounds per square inch was obtained, producing thereby a "synthetic crude oil."

William M. Burton,[2] in 1913, patented his process for the manufacture of gasoline, which to-day is the best known and most widely used of all cracking processes. In his apparatus communication is maintained between the still and condenser, which fact differentiates it from other processes now

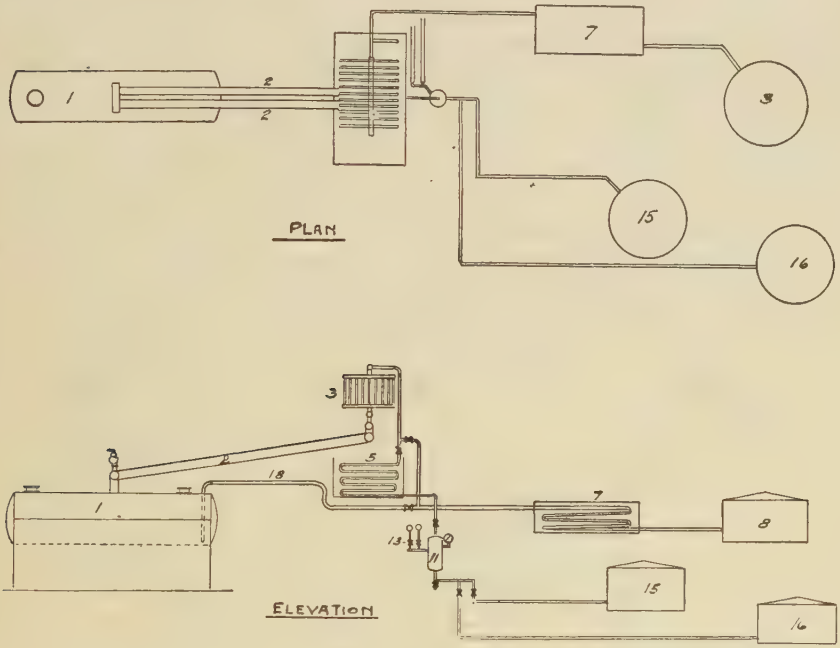


Fig. 268.

in commercial use, Dr. Burton claims high yields, less fixed gas, a sweeter product and a highly saturated gasoline. In this process, Fig. 268, the still 1 is charged with gas oil and raised to a pressure of 4 to 5 atmospheres with a still temperature of about 650–850° F. The vapors pass through vapor lines 2 to air condenser 3 where the heavier products are condensed and flow back to the still through vapor line 2.[3] The uncondensed vapors pass through the condenser coil 5, while the condensate

[1] Eng. Pat. 18,419 (1914); 100 (1915); Int. Conv. Nov. 11, 1913.

[2] U. S. Pats. 1,049,667, 1,055,707 (1913); 1,105,961 (1914); Under Int. Conv. July 3, 1912; Eng. Pat. 29,862 (1912); Fr. Pat. 469,689 (1914); Can. Pat. 155,567 (1914).

[3] Humphrey's Pats. U. S. 111,970, 1,122,002, 1,122,003 (1914); Fr. Pat. 476,782 (1914); Eng. Pats. 21,273 (1914); 7541 (1915).

passes to metering tank 11, and thence to the receiving tanks 15 and 16. About 50 per cent of the charge is distilled while the residue is pumped through the cooler 7 to the receiving tank 8. The pressure is maintained by the valve 13. When Burton stills are run in batteries, the pressure is usually maintained throughout the entire system by means of fixed still gas.

The Standard Oil Co. uses the Burton process extensively, and has used in conjunction with it several other patented installations, such as the Clark tube still (similar to the Heire water-tube boiler), in which all oil exposed to direct fire is contained in 4-in. tubes, the large drum acting as a circulation and expansion chamber. The efficiency of this still is evidently due to the increased heating surface and circulation. Where this still is employed, it is customary to conduct the run as a semi-continuous operation by feeding fresh gas oil into the still as the distillation progresses.

The Burton process as conducted in the shell stills produces approximately 30 per cent of 60° Bé. gasoline and about 3 per cent of fixed gas. The gasoline is rather highly unsaturated, and, before treatment with sulphuric acid, possesses a strong " cracked " odor.

The shell still used in the Burton plants was patented by Humphreys[1] (see Fig. 269). Still *A* is provided with false bottom *B*, which, it is claimed,

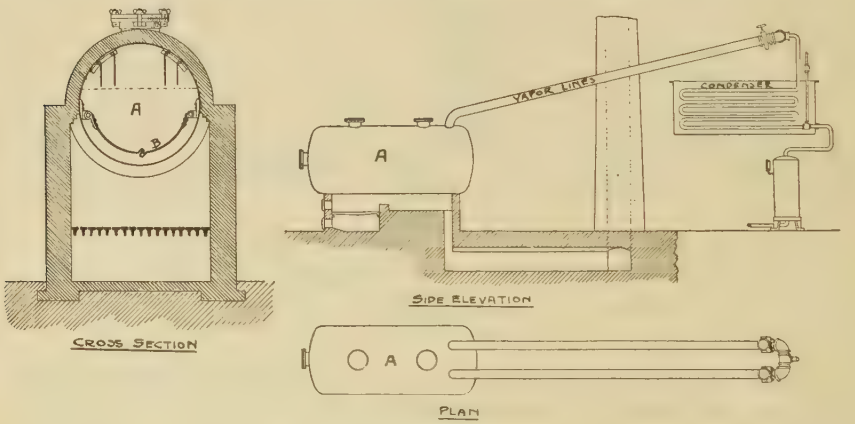


FIG. 269.

acts as a catalyst. Humphreys claims that stills equipped with false bottoms greatly accelerate the conversion of heavy oils into lighter products, and that 65 to 75 per cent of the charge may be distilled off before cleaning the still, whereas with stills not so equipped, only one-third of the charge can be driven over. Plan Fig. 269 shows the Humphreys vapor lines for condensing and returning to the still that part of the vapor which is heavier than gasoline. For a still 8 ft. in diameter and 30 ft. in length, vapor pipes 40 ft. long are recommended.

[1] U. S. Pats. 1,119,700, 1,112,003 (1914).

In 1914, Bacon and Clark [1] decomposed heavy hydrocarbons by distilling them under a pressure of 100–300 pounds per square inch. J. L. Gray,[2] passed gas oil or other heavy oil into molten lead maintained at a high temperature, thus producing low boiling-point hydrocarbons.

In 1915, Bacon, Brooks and Clark [3] proposed a vertical retort, distilling under a pressure of 60–300 pounds per square inch and at a temperature of 350–500° C.

In 1915, The New Process Oil Co.[4] decomposed oil by distilling it with

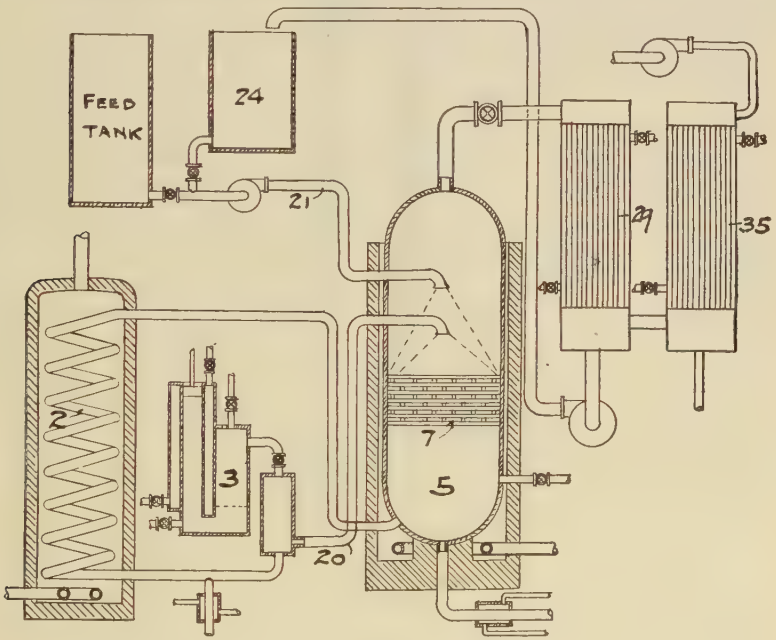


FIG. 270.

water in a retort at 340–510° C. and condensing the resulting vapors under a pressure of 3 to 5 atmospheres.

In 1915, Thompson [5] decomposed heavy oil under pressure in the presence of hydrogen and finely divided nickel.

Danckwardt,[6] in 1915, proposed to spray a heated liquid such as molten lead, sodium nitrate or hydroxide into the oil contained in the distilling vessel, under a pressure of 125 pounds per square inch and at a temperature of 400° C. The molten metal or fused salt is continuously withdrawn, reheated and delivered to the distilling vessel (see Fig. 270). The lead is heated in the coil 2 and forced in the form of a spray through the pipe 20

[1] U. S. Pat. 1,101,482 (1914).
[2] Can. Pat. 153,966 (1914).
[3] U. S. Pat. 1,131,309 (1915).
[4] U. S. Pat. 1,138,266 (1915); Eng. Pat. 4856 (1915).
[5] U. S. Pat. 1,160,670, (1915).
[6] U. S. Pat. 1,141,529 (1915).

into the still 5. The oil enters the still 5 also in the form of a spray through feed pipe 21 and commingles with the molten metal trickling through the grating 7, thus causing a destructive distillation of the oil. Carbonic acid gas at the same time is forced through the condenser coils 29 and 35 to dispel the air and permit expansion of the gases.

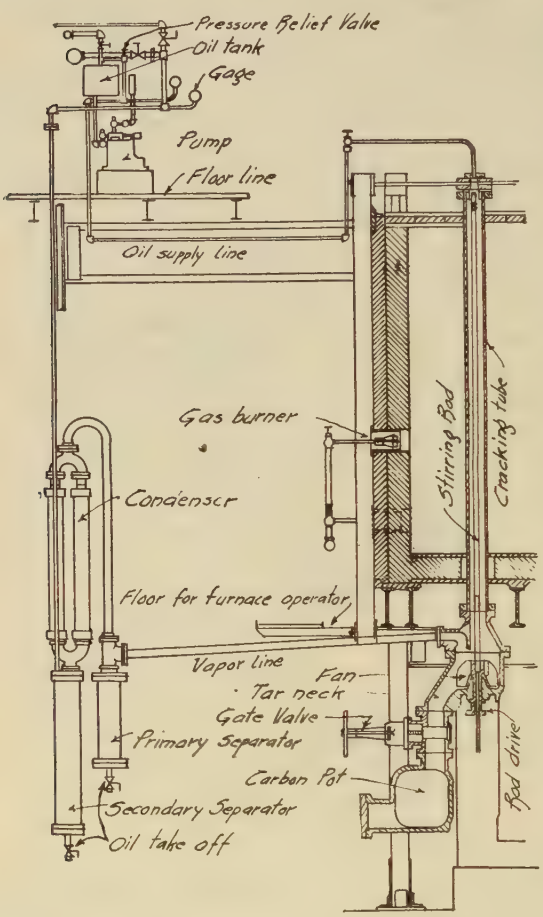


DIAGRAM OF FURNACE CONNECTIONS.

FIG. 271.

The heavier hydrocarbons (mostly burning oils) are condensed in condenser 29 and pumped to rerun tank 24. The naphtha is condensed in condenser 35 and run to the receiving tank.

In 1916 Wells[1] patented a process in which the oil vapors are passed into a bath of molten lead heated to 540° C.

In 1916, Palmer[2] decomposed the oil under a pressure of 60–400 pounds per square inch at a temperature below 200° C., then released the pressure and distilled under ordinary pressures.

The Rittman[3] process for the manufacture of gasoline, benzene, and toluene from petroleum has received much attention during the past few years. This process has been granted letters patent in England. Previous to this time patents were taken out by others for the production of aromatic hydrocarbons by cracking.[4]

[1] U. S. Pat. 1,187,874 (1916).

[2] U. S. Pat. 1,187,380 (1916).

[3] Bull. 114, Bureau of Mines (1916); J. Ind. Eng. Chem. 8, (1916), 351; Oil Paint and Drug Reporter, 89 (1916), 7, 8; J. Ind. Eng. Chem. 7 (1915), 945; J. Ind. Eng. Chem., 8 (1916), 20.

[4] Hlawaty and Friedman, Eng. Pat. 2242 (1820); Ger. Pat. 51,553 (1888). Dvorkovitz, Eng. Pats. 7983, 19,641, 21,647 (1892). Smith, Eng. Pat. 7605 (1893). Young, Eng., Pat. 12,355 (1893). Meikle, Eng. Pat. 23,649 (1896). Meffert, Ger. Pat. 99,254 (1897).

The apparatus as originally planned, Fig. 271, consists of furnaces heated by 22 gas burners, with 2 rows of 5 vertical cracking tubes 8 in. diameter by 11 ft. 6 in. long. Each tube is connected to a separate oil supply and condenser. The carbon formed on the tube walls is removed by means of chains fastened spirally to the rotating stirring shaft and falls to the bottom when it is collected in the carbon pots. A fan attached to the lower end of the stirring shaft prevents carbon from filling the bearings.

The oil is fed into the top of the tubes at a rate of 30 gallons per hour and subjected to a temperature of 700° C. at a pressure of 150 pounds per square inch. The vapors pass through the vapor line to the primary separator where the heavier products are condensed.

The lighter vapor thus passes through the condensing coil, and from this into the secondary separator where it is stored until the run is completed. A gate valve is placed between the tar neck and carbon pot, which may be closed in order to maintain the pressure while the carbon pot is being cleaned. The large percentage of fixed gas given off is usually sufficient to run the burners.

Both apparatus and process have been improved since the construction of the first unit and at this writing several commercial plants are being operated.

The Rittman process when operating on kerosene is said to yield 35 per cent of 51° Bé. gasoline which contains 10 per cent of unsaturated hydrocarbons and has the following distillation temperatures.

Initial boiling-point	60° C.
5 per cent off at	100°
35 per cent off at	150°
80 per cent off at	180°
Dry point	205°

When operated on 33° Bé. gas oil this process is said to produce 27 per cent of motor fuel of 52° Bé. and 420° F. final boiling-point, with a gas loss of 8 per cent and a loss of 3 per cent on treatment with sulphuric acid.

In the Greenstreet [1] patent, oil and live steam are sprayed through an atomizer 19, Fig. 272 into a heating coil 1 which coil is enclosed in a firebrick jacket and heated to a cherry red heat by means of an oil burner 2, Expansion takes place in the condensing tanks 3, 4, 5, 6, 7, the condensate falling to the bottom from whence it is piped to collection tank 8.

The vapor from the condensing tank 7, passes through the condenser coil 9 where it is partially condensed, thence to the gasoline separating tank 10 where a further separation takes place. The remaining gasoline vapor passes through the condenser coil 13 where final condensation takes

[1] Eng. Pats. 16,452, 17,057 (1912); Fr. Pats. 446,475 (1912); 462,484 (1913); 1,110,923-4-5 (1914); U. S. Pat. 1,166,982 (1916).

place. The non-condensable gas is trapped at 14 and absorbed by the heavy oil in tanks 15 and 16.

The condensate from 10 is emptied at intervals into the still tank 11 where the temperature is raised by means of a steam coil 12. The residue

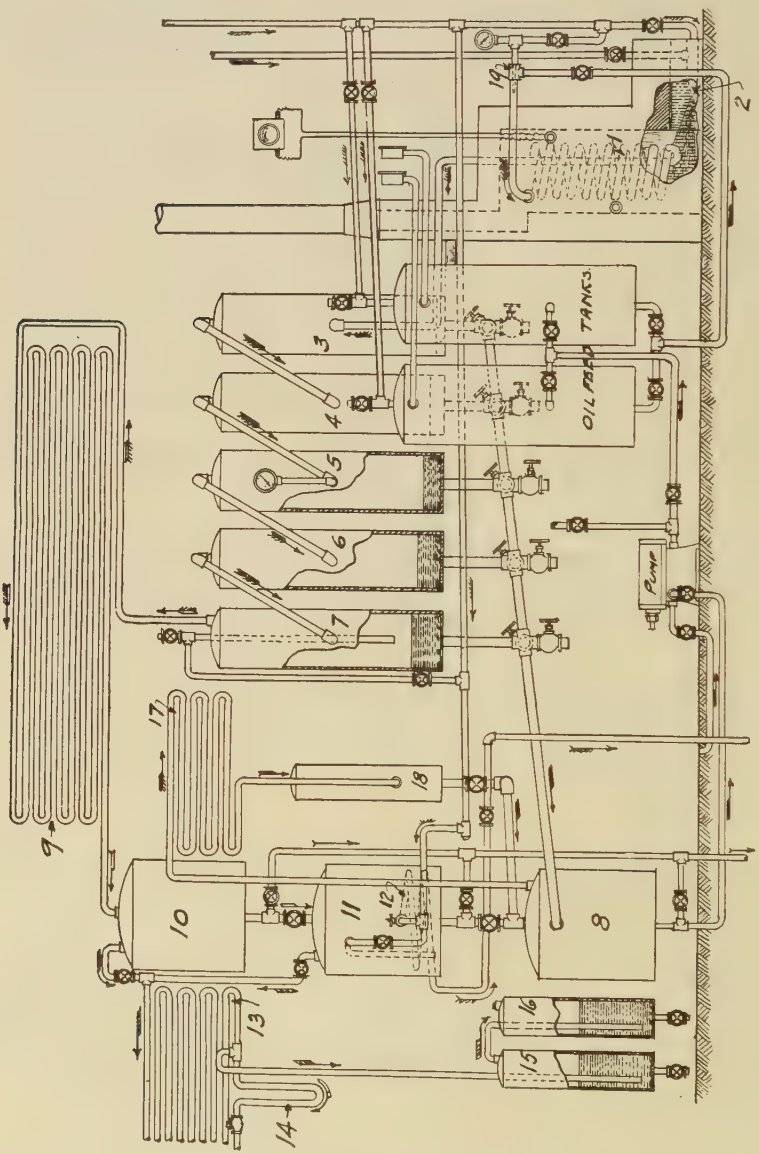


FIG. 272.

is emptied at intervals into collection tank 8 while the vapors pass through condensing coil 13.

The fraction in tank 8 is vaporized through condenser coil 17, the condensate received in tank 18 and emptied at intervals into collection tank 8.

Hall[1] devised a process for the manufacture of motor fuel of low boiling-point, for which he claims greater mileage, flexibility and ease in starting. His process consists of cracking heavy oil at a temperature of 540° C.–600° C. at 70 pounds pressure, in the tubes 4, Fig. 273. After

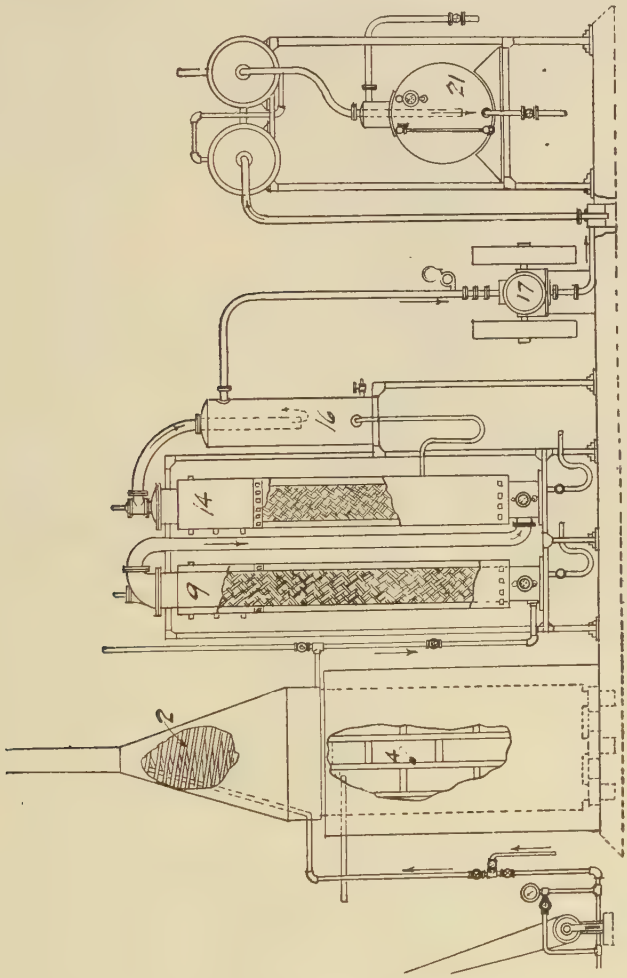


Fig. 273.

primary heating in coils 2, the vapors are expanded in a deflegmator 9, where the free carbon is caught by broken pottery and the vapor further cooled in the second deflegmator 14. The uncracked condensate obtained by this method may be reprocessed or otherwise used.

The vapor of the light hydrocarbons passes to the separator 16, and thence to compressor 17, where the pressure is raised to 100–125 pounds

[1] Eng. Pats. 17,121, 24,491 (1913); 437, 7282, 2948, 12,962 (1914); 6069, 1594 (1915); U. S. Pats. 1,175,909–10 (1916); 1,194,289 (1916); Int. Conv. May 11, 1914; Fr. Pats. 467,381 (1914); Int. Conv. Oct. 28, 1913.

per square inch. An endothermic reaction occurs with the decrease in temperature, and the condensed products pass to a receiver 21, where the fixed gas is separated and released.

The Hall water fuel is said to be quite stable, but is yellow in color and has a disagreeable varnish-like odor. It leaves a dark orange non-drying substance on evaporation. It can, however, be deodorized and rendered water white by agitating with sulphuric acid or fuller's earth. This process is being used commercially in England and America for the manufacture of "Motor Spirit."

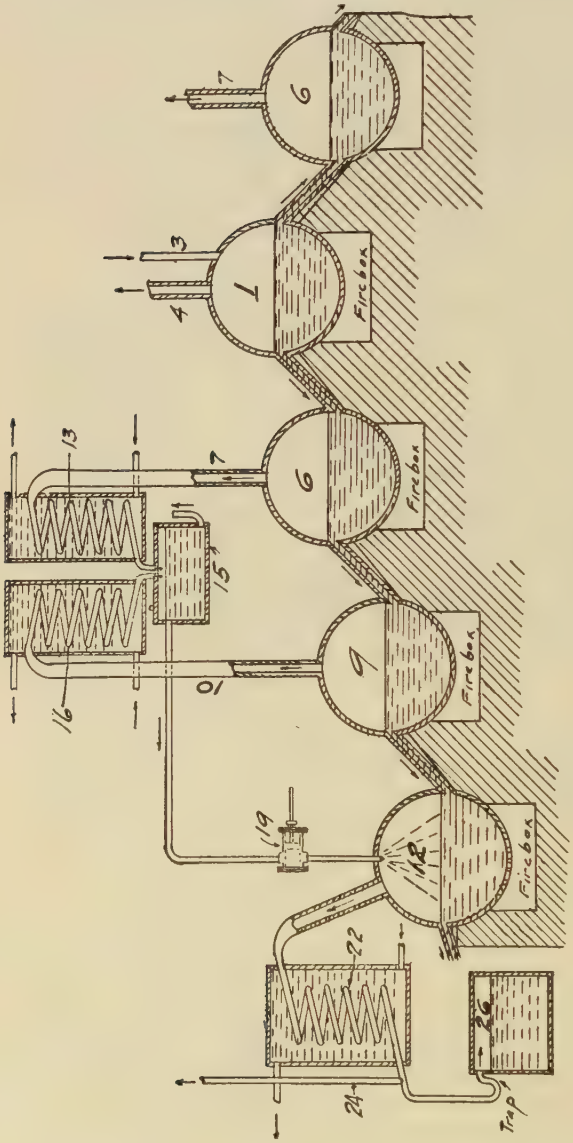


Fig. 274.

In 1916 Roth[1] devised a process of cracking, in which the crude oil is pumped continuously into still 1, Fig. 274, through charging line 3. The light distillates pass through a vapor line 4 to a condenser coil. The residue overflows to still 6 and 9, where the intermediate and heavy vapors pass through vapor lines 7 and 10 to condenser coils 13 and 16, the condensate flowing to tank 15. Any water, if present, is separated while the heavy oil rises to the top, and overflows to the pump 19 wher[illegible] forced in form of spray into another cracking still 12. Here it m[illegible]ts the hot residue which has overflowed from still 9. The vapor from still 12 passes

[1] U. S. Pat. 1,208,214 (1916).

through a condenser coil 22, where the cooling medium is kept at about 15° C. below zero. The fixed gas escapes through pipe 24, while the condensate flows to the receiver 26.

In 1914 and 1915, McAffee [1] obtained several patents in which he used anhydrous aluminium chloride as a catalytic agent. In his process, Fig. 275, the distillation is conducted at atmospheric pressure. The aluminium chloride is introduced into the still 1 through the manhole 25 and kept in suspension by means of stirring apparatus 6. The oil previously dried is

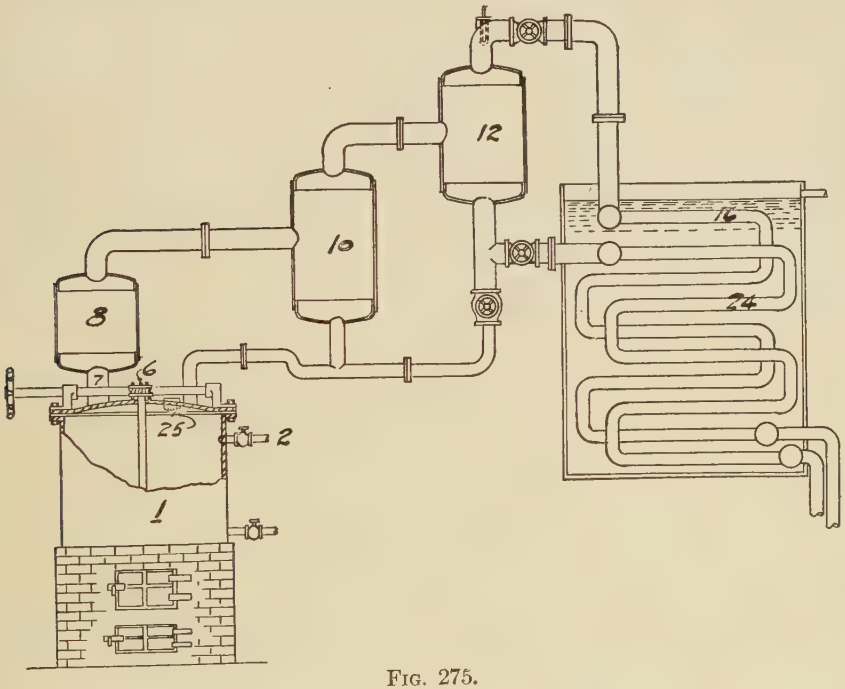


Fig. 275.

pumped into the still through feed pipe 2. The vapors pass through the vapor line 7 to the chamber 8 where any aluminium chloride carried over is arrested and drops back into the still. The vapors formed continue through this air condenser 10–12, where a partial condensation takes place.

The condensate from 10 (consisting of heavy oils) run back to the still, while the condensate from 12 (mostly solvents and burning oils) may be returned to the still or run through the cooler 24. The vapors from 12 pass through a condenser coil 16, where a final condensation takes place.

This process is similar to that of Abel's patented in 1877 and Gray's patented in 1913.

[1] J. Ind. Eng. Chem., 7 (1915), 737. U. S. Pats. 1,099,096, 1,127,465, 1,144,304 (1914); Eng. Pats. 22,243–4, 22,924 (1914); Ind. Conv. Feb. 12, 1914; Fr. Pat. 477,668 (1915).

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CHAPTER XXIII

THE DESTRUCTIVE DISTILLATION OF WOOD

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The Distillation of Wood. Wood is a material that is found widely distributed. In some sections the various woods are equally intermingled, while in other sections large areas are covered by only one species, with but few trees of other kinds. In the United States there is a yellow pine belt reaching from North Carolina to Texas, the northern limit being Central Alabama, and extending south to within a few miles of the coast. The fir belt is found on the Pacific Slope and extends from northern California into British Columbia. In Michigan are found large tracts of maple, and in other States other kinds of wood are found in quantity.

For distillation purposes, usually but two classes of woods are used—the hard woods, such as oak, beech and maple, and resinous woods, such as the yellow pine and Douglas fir. The hard woods yield larger quantities of acetic acid and alcohol and the resinous woods more tar and oils. To obtain the highest yields of the various products sought, the proper kind of wood must be selected, and the supply should be large.

Treatment of the Material Preparatory to Distillation. In hard wood distillation in the United States, the wood is cut into lengths of about 4 ft., like ordinary cord wood. In Europe the wood is often cut into short billets and then distilled. As the distillation of hard wood is now carried on mostly in connection with iron furnaces, large pieces of wood must be used in order to make a suitable charcoal.

The practice with resinous woods is very variable. Some plants use cord wood, some billets, and some chips from a chipping machine called a " hog."

In all destructive distillation processes, the finer the wood is cut the more quickly the distillation proceeds. To distil very fine material special apparatus is needed on account of the tendency of the material to pack, thus preventing the heat from passing through and also preventing the gases from escaping. Usually, in a stationary retort the wood should not be cut in pieces less than a foot in length. As the cutting of the wood requires power, labor and apparatus, the advantages of rapid distillation are often offset by the expense of preparation. For the extraction of

turpentine, the finer the particles of wood, the larger the yield, the quicker the distillation and the better the quality of the oil produced. If the residue is to be used for paper making, the chips should be of a suitable size to make the proper fiber.

Manufacturing Processes. For the production of charcoal only, the simplest and crudest form of distillation is the common charcoal *pit*, Fig. 276. This method consists of stacking up a lot of wood in a circle of 30 to 50 ft. in diameter and covering it with earth. These pits are made in various shapes and sizes. Often the wood is cut into billets and placed on end to form a circular stack of several layers, the diameter of each upper layer being less than the one immediately below it, thus forming a mound or "meiler." A passageway is left to the middle of the pile so that a fire can quickly reach the center. The pile is covered with turf and sand, except near the bottom, where vents are left for the admission of air and also for the escape of the vapors. In this form of distillation part of the wood is carbonized by the heat formed by the combustion of the other part. The water vapor is driven off first and the oxygen of the air present in the interstices of the wood is consumed. After dis-

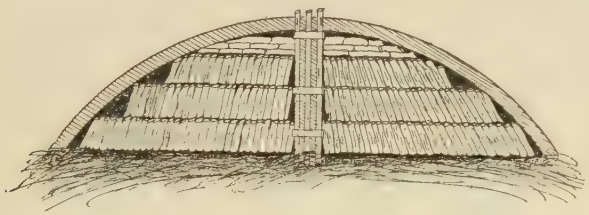

FIG. 276.—Charcoal pit.

tillation gets under way the air is carefully excluded to such an extent that only sufficient is admitted to thoroughly char the wood without burning too much of it. Any part exposed by the earth falling in is quickly covered and only cracks enough allowed to permit the gases to escape. The charring is finished when the gases become light blue in color. The earth is then removed in small sections at a time and the charcoal quenched with water.

In a charcoal *kiln* the wood is stacked either on end or lying down. A firing passage is left as in the case of the charcoal pit. The kiln itself consists of a brick chamber, either beehive in shape or rectangular. They are usually made large enough to hold from 60 to 80 cords of wood. Some are lined with firebrick part way up the side. Doors are left in the top and bottom for charging the wood. Openings are left in the bottom for the admission of air, and some have a flue connection with a stack so as to encourage the draft Those having stacks can be forced so as to complete the distillation in two or three days if necessary. Usually it takes about eleven days to charge, distill and to cool with forced draft and twenty-one days without.

An illustration of the most common form of kiln is shown with stack in Fig. 277. The method of operating a kiln is similar to that followed with a pit. The fire is led to the middle of the pile and the whole allowed to heat slowly to drive out the water, then the holes at the bottom are closed and opened in such a manner as to cause the fire to spread over the entire kiln so as to avoid, as far as possible, the formation of brands or uncharred pieces. As with the pit, the presence of the light-blue vapors denotes the fact that most of the volatile matter has been driven off. The kiln is then closed up tightly with lime and allowed to cool. In both the pit and the kiln the vapors are lost, although sometimes a condenser is used with a kiln. On account of the large amount of fire gases which mingle with the vapors, these condensers must be large and supplied with plenty of cooling water. The yield of valuable products is much less than when retorts are used.

To manufacture tar from resinous woods by means of kilns or pits, it is customary to have a trough leading from the bottom of the wood to a pit underground. The wood is cut up much finer, and is more thoroughly burnt, leaving but little charcoal, the object being to obtain as much tar as possible.

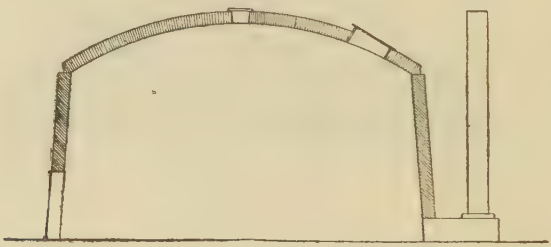

FIG. 277.—Charcoal kiln with stack.

Retorts. To save the volatile matter coming from the wood, various retorts have been devised, varying within wide limits, according to the kind of wood to be distilled. As already stated, with kilns and pits the volatile matter is lost or partially destroyed, owing to the admission of air directly to the wood.

The simplest form of apparatus for saving the vapors formed by distillation consists of an inclosed vessel, called a retort, surrounded by a suitable furnace, to which heat can be applied by means of coal, wood, oil, gas or electricity, the vessel to be supplied with a vapor pipe connecting with some form of a condenser. Some kind of tank is also needed in which to collect the condensed products. Where there is acid, the retorts are made of iron, the connecting pipes and condenser tubes of copper, and the receiving tanks of wood or copper lined. To distil with steam to obtain turpentine, a furnace would not be required, but the other apparatus would be similar.

The retorts used are of two distinct types, those placed horizontally

in the furnace and those set vertically. Of the horizontal type there are two classes, the rectangular ovens and the cylindrical retorts. Of the vertical type there are three classes, the fixed retort, the removable retort and the fixed retort with removable cage.

Most of the retorts are made of boiler plate of a thickness of $\frac{1}{2}$ in. or more. Formerly cast-iron and clay retorts were used, but, although they do not burn out as readily as wrought iron, they must be made thicker to have the same strength, and have the further disadvantage of cracking when heated.

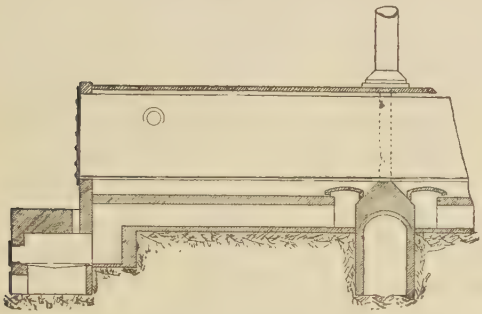

Fig. 278.—Steel oven.

Of the horizontal retorts the ovens are the most numerous — Fig. 278. They are rectangular in shape, flat on the bottom and slightly arched on top. The bottom is supplied with rails. On the sides or back are one or more openings for the exit of the vapors to be condensed. The wood is loaded on steel cars holding about two cords each and rolled into the retort. The ovens are about 6 ft. wide and 7 ft. high and of various lengths to hold two, three or four cars each. One or two coolers are used with each of these ovens, of similar shape to the ovens but of lighter material, into which the car of charcoal is withdrawn soon after the end of the distillation.

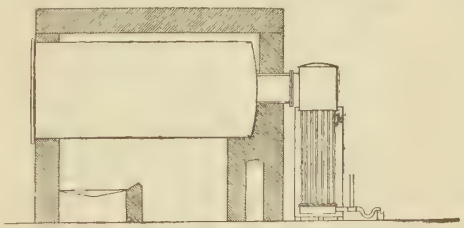

Fig. 279.—Cylindrical retort and condenser.

Some of the cylindrical retorts, Fig. 279, are made 9 ft. long by 50 ins. in diameter and will hold about a cord each. These retorts are charged and emptied by hand. An iron box mounted on wheels is used to hold the hot charcoal, and when full it is covered with a sheet-iron cover and the edges luted with sand or clay.

Of the vertical retorts no particular type seems to have the preference. The retorts are usually made cylindrical and hold from $\frac{1}{2}$ to 5 cords of wood. A convenient size is about 2 cords. The *fixed retorts* remain in the brickwork and are attached to the vapor pipe of the condenser by one or two pipes, preferably one at the top and one at the bottom. The *movable retorts* are so arranged that they can be pulled out of the furnace when the wood is charred and allowed to cool unopened. Instead of hoisting the retort itself some types use a retort with removable cage, Fig. 280.

Only the cage is removed, and as the cage does not have to stand the direct heat of the fire, it can be made of lighter material than the retort and the removing of the cage instead of the retort saves the wear and tear of the brickwork. In addition to this the vapor pipes are not disturbed.

The larger sizes of vertical retorts require suitable hoisting apparatus in order to charge the wood, and there is always danger of a rope breaking, thus causing much damage. The vertical retorts are much easier to charge and are easier to clean out than the horizontal ones, particularly while hot. They have been used for making charcoal of high carbon content.

Condensers. The condensers used are generally of one type, although other kinds might be used. The most satisfactory seems to be the vertical tubular condenser which is shown in Fig. 280. It consists of a vapor pipe, leading to an expanding chamber at the top of the condenser; the necessary condensing tubes, and a bottom chamber for collecting the condensed matter from the tubes—these parts all made of copper. The whole is contained in an iron or wooden shell which holds the condensing water. The top of the condenser is supplied with a cap or removable top fastened by means of a yoke or bolts so that the tubes can be easily reached and cleaned. To the lower chamber is connected an outlet pipe which is usually supplied with a "goose neck" or U bend, to hold back the gases, and a top opening to permit the gases to escape to the furnace. The bottom of the condenser is made sloping so as to drain out the tar. A few fractionating elements have been tried to remove the tar from the vapors, so as to make the pyroligneous acid free from tar, thus saving one distillation when making gray acetate of lime.

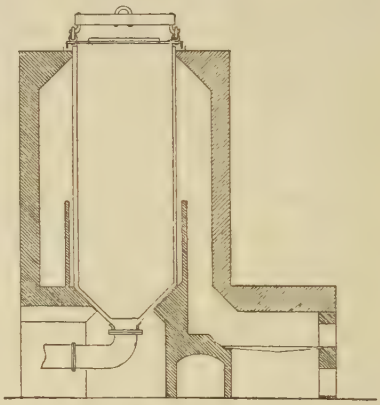

FIG. 280.—Vertical retort with removable cage.

Worm condensers have been used, and also tubes set one above the other, with removable ends, but they are not as satisfactory as the tubular condenser.

Hardwood Distillation. Using hard wood, destructive distillation is practised, the products being charcoal, acetates and wood alcohol. Most of the lately erected, large sized plants use the oven type of retort while some of the earlier constructed plants continue to use the small cylindrical type, and one or two the vertical type. Some large installations are said to have been made, using an oven type with chambers on each side of the oven for receiving and discharging cars of wood and charcoal respectively. An attempt is being made to introduce special retorts for distilling sawdust.

To carry out the *operation* of *destructive distillation* no definite rule can be followed. Some operators find that the temperature required varies with the different woods, and the time of distillation varies with the temperature. Some woods distil easily and others with difficulty. The yield of condensed products varies greatly with the method of firing. The charcoal made at a given temperature also varies in composition, according to the kind of wood used The proper conditions should always be determined by experiment when a new variety of wood is used.

To operate to the best advantage it is best to heat slowly after the liquid starts to flow from the mouth of the condenser, as overheating causes a loss of volatile matter. After reaching a certain temperature, which can be ascertained by the use of suitable pyrometers, the heating can be increased quite rapidly in order to drive out the heavy tars. The first distillate begins to come over at about 320° F. and consists of furfural, water and very little acid. The watery distillate is known as "pyroligneous acid." The percentage of acid increases with the temperature until the tar begins to distil, then it begins to drop off slightly. Meanwhile uncondensable gases are formed and these are piped to the furnace and burned. During the early stages of the distillation the color of the flame of the burning gases is blue, due to the carbon monoxide present, while later the color becomes yellow, due to the presence of the heavier hydrocarbons. The end of the operation is indicated by the falling off of the quantity of the distillate at the mouth of the condenser, by the temperature inside the retorts (about 800° F.), and by the color of the shell of the retort. The character of the distillate also indicates the end of the distillation, the tarry products being strongly in evidence. When cars or cages are used the charcoal is withdrawn hot, thus saving the heat of the brickwork for the next charge. The conditions should be regulated so that each retort can be charged once every twenty-four hours.

The Distillation of Resinous Wood. The distillation of resinous woods requires retorts varying in size and shape with the methods of operation and the products sought. The chief commercial products obtained by the distillation of resinous woods are turpentine, tar and charcoal. Soft woods yield an acid solution much weaker in acetic acid and alcohol than hard woods, thus the proportion of water distilled is greater. On this account the pyroligneous acid from resinous woods is not usually saved.

There are several methods of treating resinous woods to obtain the various products. The apparatus in the various cases varies somewhat. The methods are as follows: 1. Destructive distillation, with or without steam. 2. Steam distillation. 3. Distillation of turpentine by means of hot rosin. 4. Extraction by means of hot water. 5. Extraction by means of volatile solvents.

The destructive distillation of resinous woods is carried on in a very similar manner to the treatment of hard wood. So far, both horizontal

and vertical retorts have been used, varying in capacity from 1 to 5 cords. Various-shaped retorts have been used, and points of advantage claimed for each one. Often the retorts have been fitted with pipes and valves, so that the vapors can be drawn off successively at different levels according to the relative gravity of the condensed products.

Several unsuccessful plants have operated with retorts arranged in this manner, the idea being to draw off the tarry vapors at the bottom during the later stages of the operation, the light vapors having been previously drawn off at the top. One of the few successful distillation plants has used a modified arrangement of this system.

The greatest variation seems to be in the method of extracting the turpentine. As this substance is apt to become contaminated with tarry

AA. Retorts;
BB. Condensers;
CC. Pipe for condensed products;
DD. Receiving tank, crude liquors;
E. Oil tank;
FF. Acid and lime lee stills;
G. Neutralizing tank and filter press;
HH. Steam pans for acetate;
I. Finishing pan for acetate;
JJ. Rectifying still for alcohol;
K. Crude oil and tar still;
L. Washer for crude oil;
M. Column still to refine turpentine from crude wood oil.

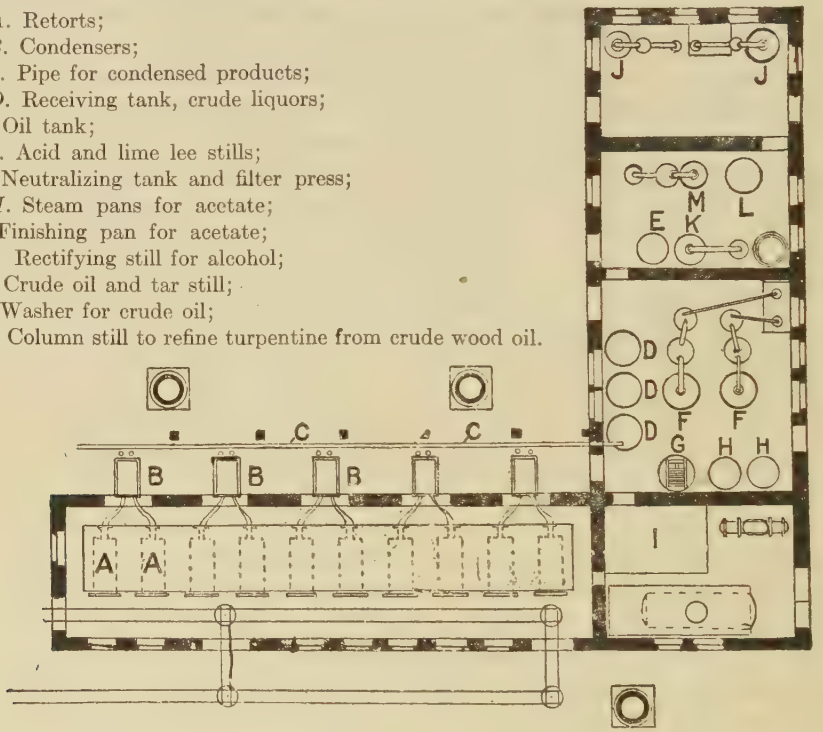

Fig. 281.—Plan of complete plant for distillation of resinous woods.

products, giving it a bad odor and color, considerable care is necessary to produce it. To avoid this contamination, some use two condensers, one for the turpentine and the other for the tar and pyroligneous acid. Others collect the turpentine in one tank and the other products in another. Usually the change from turpentine to the other products is made when the temperature reaches 320° F., or when the wood begins to decompose.

The operation is carried on at first at a low temperature so as not to

char the wood. The turpentine and resin exist already formed and are not products of the decomposition of the wood. By the influence of heat the turpentine distills, carrying with it part of the resin. Sometimes steam is added to help carry over the vapors by lowering the boiling-point. As the heat increases part of the resin decomposes and rosin oil distills over. When the wood begins to char, the pyroligneous acid begins to form and the distillation is carried on from this stage exactly as in the

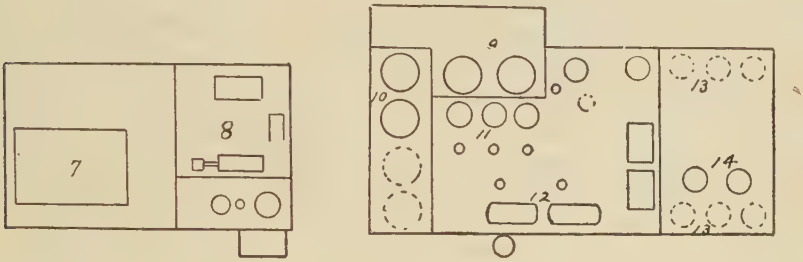

Fig. 282.

case with hard-wood distillation and the products all collected in one tank. See Figs. 281 and 282 for complete details of plant for destructive distillation of wood.

Plans of an American hard-wood distillation plant are shown in Fig. 283. Furnaces with two ovens each are shown at 1, 1, 1, 1. The wood

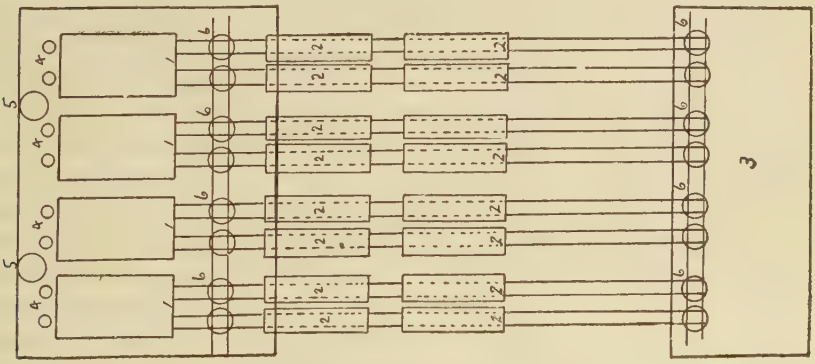

Fig. 283.

is brought to the turntables 6, in special cars. These cars are shoved into the ovens and the doors of the ovens closed. The vapors from the distilling wood are condensed in tubular condensers 4, and the condensed liquors collected in tanks 5. The cars of charcoal are pulled while hot and taken to a series of coolers, 2, 2. The charcoal stays in each cooler twenty-four hours. It is then dumped into shed 3. At 7, 8, is the boiler house containing boilers, engines and pumps.

In the refinery building at 10 are the collecting and settling vats. At 11 are shown the acid and tar stills with condensers. The lime lee stills are shown at 12. The alochol tanks are shown at 13 and the alcohol stills at 14.

The Steam Process. To extract the turpentine, which is already present in the wood, it is only necessary to employ such agents as will volatilize it. A mixture of turpentine and water boils at 95° C., so if steam be passed through chipped wood in a suitable retort and the temperature maintained above 95° C., a mixture of oil and water vapor will distill and can be condensed in the ordinary manner. This is an old method of distilling finely divided wood that has been given much attention recently. Much ingenuity has been used to devise suitable mechanical arrangements for carrying on the process successfully. The requirements are a wood chipping and elevating system that will deliver the wood to the retorts; an easy method of discharge from the retorts, for the steamed wood; and the proper conveying machinery to remove the discharged chips to a bin or to the boilers. Considerable steam is needed for this process.

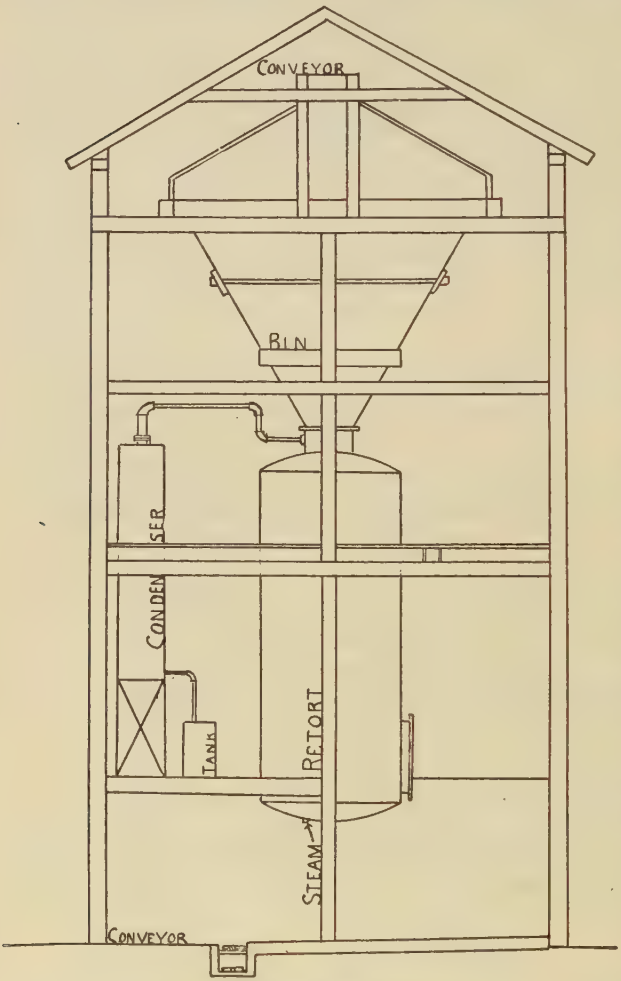

FIG. 284.

Usually, a vertically placed or slanting retort (see Figs. 284 and 285) is used with an opening on top for the entrance of the wood, and with a large discharging device at the bottom. Various forms of

rotating retorts are also used. The retorts are connected to suitable condensers.

The resinous wood is hogged, then elevated by means of a conveyor to the retorts or to a bin above the retorts. The retort is filled nearly full with wood and the opening at the top closed. Steam is allowed to enter and when the retort becomes warm enough the steam and oil vapors are led off to the condenser. A pressure of from 5 to 20 lbs. is generally maintained, so as to force the steam into contact with all parts of the wood. As the temperature is not high enough to affect the wood fiber, this process presents one of the best methods for obtaining a clear white oil from the wood in a short time. If enough steam be used all the turpentine can be extracted in less than one hour. The commercial importance of the process seems doubtful, as the yield is not sufficient to pay for the increased cost necessary to obtain selected wood. Where a market can be obtained for the chips the process can be operated to advantage. However, the resin is lost and a process is desirable where the resin can be extracted with the turpentine.

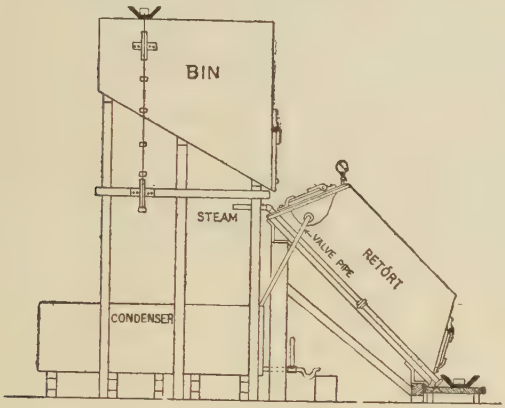

FIG. 285.—Slanting retort for turpentine.

During the digesting process, while making paper from yellow pine by the soda process, the turpentine from the blow-off at the top is condensed and recovered very economically. The product is not as good as when made by the steam process direct, the pressure being too high. With the sulphate process, the turpentine is badly contaminated and it is only recently that the oil has been purified. The oil from the sulphite process is mostly para cymene.

Resin Process. To avoid the local overheating during the early stages of the destructive distillation process, which causes part of the wood to distil before the temperature of the whole reaches 320° F., some have attempted to distil the wood in a bath of rosin. The process is said to work well, but it is doubtful if continued operation confirms first impressions. The distilling point of the resin is too close to that of wood, the rosin itself is liable to be decomposed by local overheating, and being solid at ordinary temperatures, difficulty would be experienced in pumping it and removing it from the wood at the end of the operation. It will probably have no future.

Hot Water Process. Although almost entirely experimental, this

process is of interest as it may lead to a method of extracting oleo-resins from wood without the use of expensive solvents and the entailed loss. It consists in simply heating the wood in a bath of hot water until the oleo-resins melt and float on top of the water; the water and resin are made to flow over into a tank. Although large yields have been claimed for it, it is quite evident that the process would be slow at the temperature of boiling water at atmospheric pressure. The process may be capable of development.

Extraction Processes. Of all the proposed methods for producing valuable products from resinous wood, the extraction processes seem to promise the best utilization of raw material. The oleo-resins contained in resinous pine and fir wood seem to consist of light oils, heavy oils and resins. The light oils correspond closely with turpentine, the heavier oils or pine oils seem to be oxidation products, chiefly terpineol, and the resin mostly colophony. The presence of small quantities of other products has a marked effect upon the physical properties of the chief ingredients, particularly the odor. At the present time the oleo-resins seem to be the most valuable products of the extremely resinous woods, although pulp and paper are being made from the less resinous wood.

So far the steam process has been considered the best method for extracting the light oils and part of the pine oils. By the destructive process, the remaining heavy oils and resins are converted into tar and tar oils, but usually these resins are of more value in the form of colophony.

There have been several processes advanced to extract the rosin, varying from one another in some details, but all based on the solvent power of some alkali or volatile oil. The alkali process consists in dissolving the resin in soda solution and neutralizing the solution with acid to regain the rosin. This was tried on a semi-commercial scale but abandoned in favor of the volatile solvent process. The alkali process was found to be cheaper so the plant is expected to change back to the alkali process. When solutions of alkali are used a substance called "humus" is extracted with the resin. It is only recently that a method has been found of separating this from the rosin.

The extraction with volatile solvents has been carried out on a large scale by one company and on a smaller scale by other companies. This process consists in grinding the wood, steaming out the turpentine, and extracting the remaining pine oil and resin with a neutral volatile hydrocarbon such as gasolene. The gasolene solution is distilled in direct steam heat to remove the light oils, followed by live steam to remove the heavy mineral oils and pine oils, a comparatively high temperature being maintained by steam in a closed coil. All the gasolene is not recovered, the loss being one of the chief items of expense attending the operation.

The method of extracting with volatile solvents has been known for a long time, but the low price of rosin prevented its successful application.

For a few years the price of rosin was so high that the successful development of the process became a commercial fact, but a slump in value of the rosin and turpentine produced caused at one time most, if not all, the plants to fail. With the increase in value of these products some of these plants have resumed operations.

To Obtain Refined Products. The condensed liquor from the destructive distillation processes consists of three layers, the upper layer of tarry oils, the intermediate layer of pyroligneous acid, and the bottom layer of tar. Sometimes with resinous woods the line of demarcation is not very well defined. In such cases the separation is difficult, without distilling. A centrifugal separator could be used to advantage. By heating the mixture a complete separation will usually take place.

The crude product coming from the wood in the steam process consists of crude turpentine as an upper layer and of water as a lower layer. In all the processes the separation is effected as far as possible by gravity, the different products being drawn off at the respective levels, or one drawn off after the other.

Crude Acetates. The pyroligneous acid contains fatty acids, chiefly acetic, varying from 3 to 4 per cent, about 1 to 12 gals. of wood alcohol to the cord of wood used, some acetone, light oil, metacetone and other ketones, aldehydes and tarry products. To obtain the various products, different means are pursued according to the quality of products to be made. These are brown acetate of lime or lead, gray acetate of lime, acetate of soda, acetic acid and refined wood alcohol.

To make brown acetate of lime, the acid is simply neutralized with lime and the insoluble tarry products produced skimmed off. The solution of acetate is distilled in an iron or copper still until the wood alcohol is collected, then the remaining liquor is evaporated to dryness and partially charred to destroy tarry matters.

To make gray acetate of lime, the liquor is sent to an acid still, a copper still without special fractionating column. The alcohol and acid are distilled and condensed together, a residue being left in the still amounting to about 5 per cent of the pyroligneous acid. This residue is called " boiled tar " and is removed at intervals as it accumulates.

The acid condensate is neutralized with lime and allowed to settle. The clear liquor is distilled in a " lime lee " still, an iron still with or without a special fractionating column. In this still the alcohol is distilled from the acetate liquor, the distillate containing about 8 to 10 per cent of wood alcohol. The acetate liquor is withdrawn from the still and evaporated in an open steam pan to a thick paste, which is removed to the acetate floor on top of the ovens, where the heat of the ovens finishes the drying. Some finish the drying in chambers heated by the waste furnace or retort gases.

It is possible to make acetate liquor direct from the acid still by passing the vapors through vessels containing lime and this is sometimes done.

By keeping the acetate liquor thus formed, at a suitable temperature, the alcohol vapors will pass on and can be condensed separately.

Further improvements in manufacture are now being introduced, particularly the use of multiple-effect evaporators for the evaporation and distillation of the acetate liquor and pyroligneous acid.[1]

Acetate of soda is made in a similar manner to acetate of lime. Sodium carbonate is added, in small portions at a time to avoid too much effervescing, to distilled wood vinegar until the acid is neutralized. The tarry substances appearing on the surface are removed and the brown fluid, after clarifying by standing, is drawn off into shallow iron pans which are heated by the fire gases from the retorts or by steam. The liquid is boiled down to 1.23 sp.gr. then crystallized in sheet-iron boxes.[2] The crystals are drained from the mother lye and then centrifuged. By calcining these cyrstals, redissolving and recrystallizing a very pure salt is obtained. Sometimes the solution is filtered through bone-black or boiled with 10 per cent of bone-black and after recrystallizing and centrifuging an entirely pure salt is obtained.

The simple method to produce crude sodium acetate is to neutralize pyroligneous acid with sodium carbonate, then to evaporate the solution to dryness and to burn off tarry matters. By dissolving the melted salt in water, filtering and crystallizing as above, a satisfactory product is obtained. The pure salt would be best made by using pure acetic acid solution with sodium carbonate, evaporating the solution and crystallizing.

Wood Alcohol. The crude wood alcohol is treated with lime and settled, the clear liquor being redistilled in column stills until of about 82 per cent by volume. By again redistilling, a product of 92 to 95 per cent can be easily obtained. However, to make alcohol that is miscible with water, it is advisable to dilute the alcohol with water until the specific gravity reaches 0.934 and allow the mixture to rest for a few days, when the greater portion of the hydrocarbons separate as an oily layer on the top and can be drawn off. The alcoholic fluid left is redistilled over lime and makes strong alcohol that does not become turbid upon the addition of water. The oily fractions are mixed together and redistilled separately, when a further quantity of alcohol is obtained. By treatment of the strong alcohol with chemicals, such as caustic soda and sulphuric acid before redistilling a great many of these impurities can be removed. The acetone and allyl alcohol can be separated from the wood alcohol by repeated fractional distillation being found in the first and last runnings respectively. Only the portion miscible with water is saved, the other portions being worked over. The first runnings of the distillate are more or less colored, but the middle fractions are colorless and yield good alcohol. After the middle portion distills the alcohol begins to contain oil and it

[1] Forest Service Circular, "Distillation of Hardwood," R. C. Palmer.

[2] Brannt, "Manufacture of Vinegar."

becomes non-miscible. Subsequently, the distillate becomes turbid and finally a mixture of oil and water comes over, which separates into two layers. To remove all traces of acetone the following methods can be used. One is to form a compound of wood alcohol and calcium chloride, which is stable at 100° C.[1] By gently heating, the acetone is driven off, and then by adding water and raising the temperature to 100° C. the calcium chloride compound decomposes and the methyl alcohol distills. Another method is to add caustic potash and iodine until the yellow color disappears, then to distill.[2] The watery alcohol is repeatedly rectified over lime, and finally over metallic sodium or phosphoric anhydride to remove the last traces of water.

The Crude Tar. The tar from hard woods is usually burned for fuel, but that which is to be utilized is washed with water or dilute milk of lime, in order to wash out the acid. It is then ready for further treatment. The tar from resinous woods is distilled with live steam in a copper tar still until the oils are removed. If these oils contain turpentine as they would when the distillate is collected together, they are specially refined. When thick enough the tar is ready for barreling.

Tar Oils. There is a small but increasing demand for tar oils as insecticides and disinfectants. To obtain tar oil from the tar it is distilled in a wrought or cast-iron vessel sometimes provided with a stirrer. The general shape of the still may be similar to a turpentine still, Fig. 291, or the still may be a horizontal cylinder set in brick work. The still is heated slowly and the distillate collected until the specific gravity of the tar oil reaches about 0.98 when the receiver is changed Some of the oils present in the tar distill unchanged while the heavier products are broken up to a greater or lesser degree, forming coke and gas. Following the light oils, a heavy oil comes over, having a specific gravity of upwards of 1.01 and of a yellowish green color. The distillation is sometimes carried on until nothing but coke is left in the still but it is usually better to stop with the production of pitch which can be drawn out hot from the still. This is run out on iron plates to cool, care being taken to prevent ignition. The condensate is sometimes divided according to the temperature of distillation, the light oils being collected up to 240° C. and the heavy oils between 240 and 290° C.[3] The heavy oil contains most of the creosote, which is extracted from the heavy oil by means of caustic lye of about 1.2 sp.gr. The hydrocarbons are boiled out and the creosote separated by neutralizing with sulphuric acid. The treatment is repeated and the final creosote distilled, the product coming over between 200 and 220° C. being called commercial wood creosote. To further purify it, it is oxidized with a mixture of dichromate of potassium and sulphuric acid and again distilled.

[1] Thorpe, "Outlines of Industrial Chemistry."
[2] Brannt, "Manufacture of Vinegar."
[3] Thorpe, "Dict. of Applied Chemistry."

The crude oil in the distillate from the steam treatment of pine tar is often saved. It varies in color from light yellow to brown, exposure to the air causing the color to become much darker. A number of substances are present, including the oils coming from the distillation of the turpentine and from the destructive distillation of the resin in the wood. The crude oil also contains considerable quantities of creosote and tar products. To remove these, the oil is redistilled in a still of similar shape and construction as the tar still—only smaller. Fig. 286. The oil comes over with only a slight coloration. To prevent this color, the crude oil is sometimes treated with chemicals such as caustic soda, lime, permanganate, sulphuric acid and the like before being distilled. These substances usually fail to remove either odor or color to any great extent. When the percentage of turpentine in the wood oil is large, the crude oil is washed with water or alkali in an agitator and often distilled in a column still similar to the still used in refining wood alcohol.

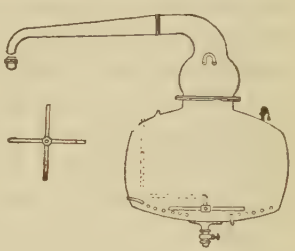

FIG. 286.—Turpentine and tar still.

Turpentine. The crude wood turpentine caught separately when wood is distilled by any method, is usually refined in order to make a marketable article. When the oil is very impure a still with a short column is desirable. When the oil is relatively pure and almost colorless like that obtained in the steam distillation, a simple distillation is all that is needed. Fig. 286. The oil should be tested as it comes from the still and when the specific gravity reaches 0.875 the receiver should be changed or the distillation ended. The distillate is often divided into three portions, the first fraction consisting of the light oils, corresponding to turpentine, the second fraction being a mixture of turpentine and light pine oils and the third fraction being very heavy pine oils. The middle fraction is redistilled and yields an additional amount of turpentine. A heavy oil called pine oil remains behind, which can be distilled at a higher temperature. This oil should not be mixed with the turpentine, as the mixture does not dry readily.

Sometimes the turpentine is treated like crude oil, with caustic soda, sulphuric acid and permanganate, but such treatment is not desirable if it can be avoided. The crude oil is sometimes washed in a vessel fitted with stirrers.

Pine Oils. The heavy oils accompanying wood turpentine are called pine oils. They are divided into two grades, water white and yellow. The darker grades are heavier and are of the most value. They are used in medicine and as solvents. Terpineol is one of the chief ingredients.

Acetic Acid. This acid is not usually prepared directly from wood vinegar, although it could be with considerable trouble and expense. It

is usually prepared by the decomposition of some acetate by means of a mineral acid.

Although formerly hydrochloric acid was extensively used for this purpose, owing to the disadvantages of using sulphuric, at present sulphuric acid is used. Sulphuric acid with acetate of lime leaves a residue of gypsum which is a poor conductor of heat and very insoluble in water. The gypsum also retains considerable acetic acid at moderate heats. To gain all the acid it was necessary to use a high temperature in a fire-heated still. This caused decomposition of the sulphuric acid and distilled part of the tarry substances.

To overcome these difficulties the gray acetate of lime is placed in a shallow cast-iron still heated by means of high-pressure steam. The still is supplied with scrapers and stirrers. A vacuum is maintained toward the end of the operation and thus the acetic acid is removed at a lower temperature. If properly worked such a still will make a yellow acid showing as much as 80 per cent total acid.

The acid is not pure. Further distillation in a simple still improves it. For the manufacture of stronger and better acid, the distillation is carried on in column stills. The first runnings will be weakly acid, containing acetic, propionic and butyric acids. A middle fraction will yield 99 per cent acetic acid with a melting-point of 14 to 16° C.

To pass the pharmaceutical test it is necessary to add potassium permanganate to the glacial acetic acid and again distill. The permanganate oxidizes empyreumatic substances and also any sulphurous acid that may be present.

Usually, it is best to start with acetate of lime or soda and to distill with concentrated hydrochloric acid in a copper still, care being taken to have an excess of the salt in the still. When brown acetate of lime is used, it is previously roasted at a low temperature. The acid formed is colored and contains about 50 per cent of anhydrous acid. With dilute hydrochloric acid in the still, the acetic acid is purer, but contains only 30 per cent anhydrous acid. Often the acid is distilled in Marx vessels and filtered in towers through freshly burned charcoal. To obtain stronger acid, the weak liquor is redistilled in column stills and the stronger parts of the distillate caught separately. Any HCl that may be found in the distillate can be removed by rectifying over acetate of lime or soda. Sulphuric acid could be used to effect the distillation, but the operation is not so smooth and the distillate is apt to contain sulphur dioxide.

Glacial acetic acid can be prepared by distilling 12 parts by weight of pure anhydrous sodium acetate with 11 parts of concentrated sulphuric acid in cast-iron stills provided with stirrers and scrapers and preferably under a vacuum. The strong acid is distilled in column stills. The first portion of the distillate is rectified over sulphuric acid and pyrolusite to remove traces of sulphurous acid. The last portion, which is frequently empyreumatic, is collected by itself. The water in the 50 per cent acid

can be removed by distilling with anhydrous calcium chloride and cooling the distillate, whereby one portion crystallizes. The liquid portion is drawn off and again distilled over calcium chloride. By distilling strong acid over fused and coarsely powdered potassium acetate and changing the receiver at 120° C. the glacial acetic acid will pass over in the last portion. This is again rectified over potassium acetate and the distillate cooled to about 16° C. to crystallize the acid. Stoneware vessels are needed to carry on the distillation, as the acid strongly attacks metals. Sometimes copper stills are used with silver necks and worms. An attempt is also being made to use aluminum.

Acetone. On a commercial scale, acetone is made by the dry distillation of gray acetate of lime at 290 to 400° C. in retorts which are connected with a cooling apparatus. These retorts may be fitted with shelves or may be of cast iron and provided with scrapers and stirrers. When brown acetate is used it is previously roasted at 230° C. The first runnings are weak in acetone but the percentage increases with the temperature. The distillate separates into two layers, the " heavy acetone oils " on top and the lighter oils dissolved in water on the bottom. The yield is about 20 per cent of the calcium acetate. The crude acetone is treated with a small quantity of caustic alkali or sulphuric acid or both and distilled in column stills in a similar manner to wood alcohol, a nearly pure product being obtained.

The nearly pure acetone can be purified by treatment with sodium bisulphite and crystallizing the compound formed.

Chemical Theory and Reactions Involved in the Distillation of Wood. Wood consists essentially of ligno-cellulose, with resins, sap and coloring matter. Green wood contains varying amounts of water up to about 50 per cent by weight. Air dried wood contains about 20 per cent of moisture which can be eliminated by heat, but is reabsorbed by exposure to the air. Various chemicals affect cellulose, but it is usually a very resistive substance. When burned, wood leaves an ash varying in amount with the kind of wood. Resinous woods contain in addition to the woody fiber, a large amount of resins and oils which can be extracted by solvents, leaving the fiber intact. The oil is chiefly pinene the principal ingredient of turpentine, and the resin is chiefly colophony.

Cellulose being a complex organic substance the chief influence of heat is naturally to decompose it into simpler compounds. From its composition, it would be expected that by driving off the water, 44.45 parts by weight of charcoal would be obtained. It breaks down, however, into more complex substances than water and carbon. A relatively high temperature is needed to start the decomposition and the temperature must be continually increased during most of the distillation in order to continue the decomposition.

Cellulose may be considered a hexahydric alcohol $C_{12}H_{14}O_4(OH)_6$. From the yield of charcoal the final products of distillation might be written

$$C_{12}H_{20}O_{10} = 8C + C_4H_{20}O_{10}$$
$$100 = 29.6 + 70.4.$$

The $C_4H_{20}O_{10}$ may be considered to have arranged itself in various ways in order to form the tar, acetic acid, methyl alcohol and gas. For examples of the possible changes the following are given.[1]

1. $C_4H_{20}O_{10} = \underset{\text{acetic acid}}{2C_2H_4O_2} + \underset{\text{water}}{6H_2O}.$
2. $\underset{\text{acetic acid}}{C_2H_4O_2} = \underset{\text{wood alcohol}}{CH_4O} + \underset{\text{carbon monoxide}}{CO}.$
3. $\underset{\text{acetic acid}}{C_2H_4O_2} = \underset{\text{marsh gas}}{CH_4} + \underset{\text{carbon dioxide}}{CO_2}.$
4. $\underset{\text{acetic acid}}{2C_2H_4O_2} = \underset{\text{acetone}}{C_3H_6O} + \underset{\text{carbon dioxide}}{CO_2} + \underset{\text{water}}{H_2O}.$
5. $\underset{\text{acetone}}{2(C_3H_6O)} = \underset{\text{metacetone}}{C_6H_{10}O} + H_2O.$
6. $\underset{\text{acetic acid}}{C_2H_4O_2} + CO = \underset{\text{aldehyde}}{C_2H_4O} + CO_2.$
7. $\underset{\text{methane}}{2CH_4} = \underset{\text{acetylene}}{C_2H_2} + H_6.$
8. $10CH_4 = \underset{\text{naphthalene}}{C_{10}H_8} + H_{32}.$

The products of distillation seem to be water, fatty acids, hydrocarbons, phenols, guaiacol, alcohols, aldehydes and ketones. The methyl group seems to predominate. The method of decomposition is difficult to determine and at present the yields of the various substances are the only guide. These vary much when the wood is heated rapidly and the influence of local heating is a disturbing factor. An increase of temperature inside of the retort over that in the furnace indicates that at one stage of the distillation at least, heat is evolved by the decomposition of the material inside of the retort. The analysis of the wood partly charred leads to the conclusion that while some of the acetic acid is coming off the decomposition takes place according to the following equation:

$$(C_6H_{10}O_5)_2 = \underset{\text{partly charred wood}}{2C_4H_6O_3} + \underset{\text{loss}}{2C_2H_4O_2}.$$

The gas formed at the same time comes from the acetic acid as in 2, 3, 4, 6 and 7, and the excess water from the moisture still present in the wood.

Ligno-cellulose seems to be homogeneous compound. The lignone has been given the formula $C_{19}H_2O_{29}$. It acts like a ketone with a hexene constitution, being apparently an unsaturated compound. Ligno-cellulose seems to contain the meth-oxy group ($O \cdot CH_3$) and a residue which is easily hydrolysed by both acids and alkalies to acetic acid. This acid amounts to 5 to 7 per cent of the ligno-cellulose.[2]

[1] Brannt, "Manufacture of Vinegar."
[2] "Cellulose," C. F. Cress.

Much progress is being made toward the solution of the problem of determining the composition of wood. A method of analysis is being prepared by the Forest Service.

When wood and most other cellulose materials are decomposed by heat, is seems impossible even by the use of great heat to drive off entirely the hydrogen and oxygen to produce pure carbon.

The refined products are made in accordance with better known theories. The acetates are made according to the well-known formula.

$$\underset{\text{base}}{ROH} + \underset{\text{acetic acid}}{CH_3COOH} = \underset{\text{acetate}}{CH_3COOR} + \underset{\text{water}}{H_2O}.$$

The wood alcohol is refined when distilled, according to the theory pertaining to miscible liquids, which in the case of alcohol and water would be that the boiling point is higher than the temperature at which the sum of the maximum or saturation tensions of the two separate vapors is equal to the external pressure and that at any given stage of the distillation, the alcohol is more abundant in the vapor than in the mixed liquids in the still. Thus the percentage of alcohol increases with repeated distillations.

The turpentine distils with steam according to the law of immiscible liquids, which states that distillation will take place at the temperature at which the sum of their vapor pressures is greater than that of air. The quantity of each liquid found in the distillate is proportional to the vapor density. With crude liquors, the temperature and proportions would be different because the impurities may or may not be immiscible with water and the system would be altered.

The distillation of the other products such as wood oil from tar is similar to that of turpentine, but the system is comprised of three substances, tar and oil miscible with each other in nearly all proportions and water, which is not miscible with either the tar or the oil.

Acetone is formed by the destructive distillation of acetate of lime (or other acetate) according to the formula.

$$(CH_3 \cdot CO \cdot O)_2 \cdot Ca(CH_3 \cdot CO \cdot O)_2Ca = 2(CH_3 \cdot CO \cdot CH_3) + 2(CaO \cdot CO_2).$$

The destructive distillation of the tar presents more difficulties from a theoretical standpoint than that of wood. The substances constituting it are more varied and the reactions would be more complex. It might be possible that by distilling with steam and under a vacuum, these tar bodies might be distilled and separated without decomposition.

CHAPTER XXIV

OILS, FATS AND WAXES

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Classification of Fats. The term *oil* is used for substances differing widely both in composition and properties and in this chapter the *fatty* oils only will be considered. Fats and fatty oils consist essentially of compounds of the higher fatty acids in combination with glycerol and are termed glycerides. Their composition was first placed on a scientific basis by Chevreul, who in the early part of the last century showed that when a fat, such or tallow or lard, was converted into soap by the action of sodium or potassium hydroxide, the fat was decomposed into glycerine and fatty acids, the latter combining with the alkali to form the soap, while the glycerine, remaining free, was separated in the lyes. The three most commonly occurring glycerides are stearin and palmitin (of which tallow chiefly consists) and olein (the principal constituent of olive oil). The conclusions of Chevreul as to the composition of fats were subsequently confirmed by Berthelot, who succeeded in producing the glycerides synthetically by heating the fatty acids with glycerine under pressure in sealed tubes. Heating together, for example, stearic acid and glycerine, he obtained stearin, according to the equation:

$$3C_{18}H_{35}O_2H+C_3H_5(OH)_3=C_3H_5(C_{18}H_{35}O_2)_3+3H_2O.$$

From their physical appearance it is not possible to give a definite classification, for what would be considered a solid fat in a temperate climate might be a liquid in a warmer locality. Roughly, however, we may class certain ones as liquid fats or oils, and others as solid fats, or fats.

" The most convenient classification of fats (fatty oils and solid fats) for practical purposes, appears to be given by arranging them according to the magnitude of the iodine value. This principle leads, without unduly forcing it, to a natural subdivision into liquid fats and solid fats, the former being differentiated from the latter by the considerably higher iodine value. Hence, an arrangement based on the magnitude of the iodine value would include the older system of classification according to consistency. Inas-

much as the magnitude of the iodine value stands in close relationship to the absorption of oxygen, or, in other words, to the drying power, classification on the iodine value would also include the older subdivision into drying and non-drying oils." (Lewkowitsch.)

Arranged in this manner are the following subdivisions:

I. *Liquid Fats and Fatty Oils.*

A. Vegetable oils
1. Drying oils
2. Semi-drying oils
3. Non-drying oils

B. Animal oils
1. Marine animal oils
   (*a*) Fish oils
   (*b*) Liver oils
   (*c*) Blubber oils
2. Terrestrial animal oils

II. *Solid Fats.*

A. Vegetable fats

B. Animal fats
1. Drying fats
2. Non-drying fats

Classification of Waxes. Our comprehension of the generic term "wax" is based in considerable measure on the physical characteristics of the oldest known wax; namely, common beeswax. It has been suggested that the term wax is defined as applied to more or less unctuous, fusible, variably viscous to solid substances, having a characteristic "waxy" lustre, which are insoluble in water but usually soluble in carbon di-sulphide, benzol, etc., and which are extremely suspectible to changes in temperature and whose origin, composition and color are variable.

Thus under this definition are included the class of waxy bodies which consist of mono or dihydric alcohols united with the higher fatty acids to form esters (beeswax, carnauba wax, etc.), as well as glycerides of a "waxy" appearance, such for example as Japan wax; and the hydro carbon waxes paraffin, ceresin, ozocerite and the like.

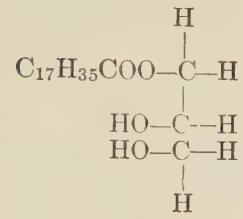
Waxes may be grouped as follows:

A. Liquid waxes

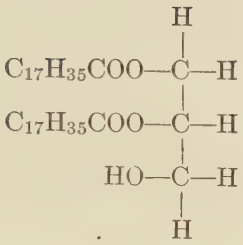
B. Solid waxes
1. Vegetable waxes
2. Animal waxes

Constitution of the Fats. The fats as stated are combinations of glycerol with fatty acids. Glycerol being a tri-hydric alcohol will combine with one, two, or three acid radicals, thus forming mono-glycerides, di-glycerides, and tri-glycerides. The last class, however, is the most important, as it is this condition which is supposed to exist in the neutral fats. The following graphic formulas will more clearly emphasize the three possible combinations:

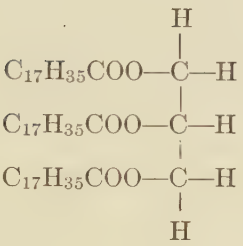
Monostearin.



Distearin.



Tristearin.



It will be seen that not only is it possible to have compounds in which one acid enters into the combination, but also others, known as mixed glycerides, in which two or even three different acid radicals may be joined to one glycerol group. This is thought by some to account for the fact that practically all of the common oils are mixtures, rather than simple esters. Our present knowledge, however, does not warrant any definite conclusion in this matter.

The fatty acids occurring in the more common oils, together with a few of their constants, will be found in the table on the following page.

The fatty acids are all lighter in weight than water. Those having less than ten carbon atoms may be distilled, and are known as the volatile fatty acids. Those containing more than ten carbons cannot be distilled without decomposition and are known as non-volatile fatty acids. The oils containing the saturated acids do not undergo any marked change when exposed to the air. On the other hand those which contain the unsaturated acids become gummy, and in certain instances when exposed in thin layers form dry, hard films. This change is called drying, and is most marked in the case of those oils containing glycerides of linoleic, linolenic, clupanodonic and ricinoleic acids.

Acid.	Formula.	C°	Sp. Gr.	Melting Point C°.	Ref. Index C°.
Saturated Acids, $C_nH_{2n+1}COOH$					
Butyric	C_3H_7COOH	20	0.959	−6.5	1.3990 at 20
Isovaleric	C_4H_9COOH	20	0.931	−51	.....
Caproic	$C_5H_{11}COOH$	20	0.924	−8	1.4163 " 20
Caprylic	$C_7H_{15}COOH$	20	0.910	16.5	1.4282 " 20
Capric	$C_9H_{19}COOH$	40	0.8858	31.4	1.4285 " 40
Lauric	$C_{11}H_{23}COOH$	20	0.883	43.6	1.4266 " 40
Myristic	$C_{13}H_{27}COOH$	60	0.8584	53.8	1.4307 " 60
Palmitic	$C_{15}H_{31}COOH$	60	0.8527	62.6	1.4269 " 80
Stearic	$C_{17}H_{35}COOH$	80	0.8386	69.3	1.4300 " 80
Cerotic	$C_{25}H_{51}COOH$	79	0.8359	78	.....
Unsaturated Acids, $C_nH_{2n-1}COOH$					
Tiglic	C_4H_7COOH		0.9641	64.5	.....
Oleic	$C_{17}H_{33}COOH$		0.898	14	1.4603
Erucic	$C_{21}H_{41}COOH$	.....	.....	34	.....
Other Unsaturated Acids					
Linoleic	$C_{17}H_{31}COOH$	14	0.9206	.....	.....
Linolenic	$C_{17}H_{29}COOH$		0.9228	.....	.....
Ricinoleic	$C_{17}H_{32}OHCOOH$	15.5	0.9509	4	.....
Clupanodonic	$C_{17}H_{27}COOH$	.....	.....	.....	.....

Liquid Fats

Vegetable Oils. The usual method of obtaining the oils is by crushing that part of the plant richest in oil, and subsequently pressing the ground pulp thus obtained. Extraction with benzine or other solvent is also employed. The crushing may be secured by means of the edge-runner, or by means of heavy steel rollers arranged in vertical series. The crushed material is then placed in canvas bags, and subjected to hydraulic pressure. The first pressing is usually done in the cold, as a lighter color and better quality is thus obtained. During the second pressing the pulp is heated, thereby producing a larger yield but of an inferior quality. By further heating a final oil is obtained known commercially as " foots." The extraction process consists in treating the ground pulp contained in closed vessels, with benzine, naphtha or other solvents. The extract is subjected to distillation in order to recover the solvents, leaving the fats in the still. Although this method gives a larger yield than is possible by pressing, it is not generally employed on account of the risk from fire, the cost of installation, and impossibility of directly using the press cake as a cattle food.

Vegetable Drying Oils. Drying oils are characterized by their power to absorb oxygen from the air, thus forming an elastic film. The amount of this absorption in the main is in proportion to the iodine value; so that we may roughly judge of the drying quality of an oil from its iodine number.

TABLE OF CONSTANTS FOR DRYING OILS

Name of Oil.	Oil Content of Seed, Per Cent.	Specific Gravity.		Saponification Value.	Iodine Value.	Refractive Index.	
Perilla	35.8	0.9306	20° C	189.6	206.1	.....	.....
Linseed	38–40	0.9315–45	15° C	192–195	171–201	1.4835	22° C
Tung	40-41	0.9360–432	15° C	193.	150–165	1.5030	19° C
Hemp	30–35	0.9255–80	15° C	192.5	148	1.4780	15.5° C
Poppy	41–50	0.9240–70	15° C	195.	133–143	1.4586	60° C
Sunflower	21–22	0.9240–58	15° C	193.5	119–135	1.4611	60° C
Tobacco seed	38–40	0.9232	15° C	170.	118.6	.....	.....

Perilla Oil. This oil occurs to the extent of 35.8 per cent in the nuts of the *Perilla ocymordes*, a plant indigenous to East India, Manchuria, and Japan. It has the highest iodine value of any known oil, and in odor and taste resembles linseed oil. Its drying quality, however, is inferior to linseed oil, due to its peculiar property of forming drops when spread on a hard surface.

Linseed Oil. This oil has been discussed more at length in the second section of this chapter. It is obtained from the seeds of the flax plant, grown extensively in Russia, India, Argentina, Canada and the United States. On cold pressing, a light yellow oil is obtained, used to a limited extent as an edible oil. By far the greatest quantity, however, is used in the manufacture of paint and varnish. The chemical composition of linseed oil is not well known, although indications point to about 10 per cent of glycerides of solid fatty acids, equal parts palmitic and myristic acids. The liquid glycerides consist of approximately 5 per cent of oleic acid, 15 per cent of linoleic acid, 15 per cent of linolenic acid, and 65 per cent of isolinolenic acid. When the price permits, linseed oil is converted by hydrogenation into a solid fat, which serves as a substitute for tallow in soap making. It is less readily hydrogenated than some other fatty oils.

Tung Oil. This oil is often spoken of as "Chinese Wood Oil." It is obtained from the seeds of *Aleurites cordata*, a tree indigenous to China and Japan. The oil varies to some extent according to its source. The seeds are usually roasted, broken into a powder and pressed. The cold pressed oil is pale yellow, and is known in the trade as "white tung oil." That resulting from hot pressing is dark in color, and termed "black tung oil." The raw oil has a peculiar odor suggestive of ham. Its chemical constitution differs from linseed in that it consists almost wholly of glycerides of oleic and elaeomargaric acids.

Tung oil is used principally in the manufacture of varnishes and linoleum. When incorporated with ordinary rosin and suitably thinned, a varnish is obtained which is not affected readily by water, while varnish made with rosin and linseed oil alone is quickly turned white by contact with water. In consequence of this behavior of tung oil, it has become

very popular with the varnish maker as a means of producing cheap but good varnish. Varnishes made with this oil and rosin ester (glyceride of the acids of colophony) are extensively used. When heated to 230° C. and over, the oil coagulates to a transparent solid which is elastic under compression, and this product has been recommended as a rubber substitute or factis. Hydrogenated tung oil expands in a noteworthy manner on solidifying from the molten state.

Hemp Seed Oil. The source of this oil is the hemp plant, *Cannabis sativa.* The color of the fresh oil is light green, becoming brownish yellow on standing. The solid glycerides of hemp oil are claimed to be those of stearic and palmitic acids. The liquid glycerides contain linoleic, oleic, linolenic, and isolinolenic acids. It is used as a paint oil, for making soft soaps, and low grades are employed for certain varnishes.

Poppy Oil. To obtain this oil the seeds are pressed cold, thus producing a product almost colorless, or very pale golden yellow, known in the trade as "white poppy seed oil." That expressed at a higher temperature is known as "red poppy seed oil." It is cultivated largely in Asia Minor, Persia, India, Egypt, and Russia. It is used largely as a salad oil, and in the manufacture of artists colors.

Sunflower Oil. This oil is obtained from the seeds of the *Helianthus annuus.* It is of a mild taste, pleasant odor, and a pale yellow color. It is raised extensively in Russia, Hungary, India, and China. It is employed in soap making, and for the manufacture of varnish. This oil does not dry as readily as those previously mentioned.

Tobacco Seed Oil. The oil obtained from the seed of the tobacco plant is of a pale greenish yellow color, and dries very readily. On account of its high price it has never found any commercial application.

Vegetable Semi-drying Oils. These oils form a connecting link between the drying oils and the non-drying oils, although it is difficult to say to which class they belong. Chemically they differ from the drying oils by the presence at the most only of small amounts of linolenic acids; and from the non-drying oils by the linoleic acid they contain.

TABLE OF CONSTANTS FOR SEMI-DRYING OILS

Name of Oil.	Oil Content of Seed, Per Cent.	Specific Gravity.		Saponification Value.	Iodine Value.	Refractive Index.	
Soja bean.....	18	0.9242–70	15° C	192.7	121.7	1.4762	15.5° C
Pumpkin seed..	35–37	0.9237	15° C	188.4	123–130	1.4723–38	25° C
Corn.....	6–10	0.9213–55	15.5° C	188–193	1'3–125	1.4750–70	15.5° C
Cotton seed...	24–26	0.9220	15° C	193–195	106–110	1.4743–52	15° C
Sesame.....	50–57	0.9230–37	15° C	189–193	103–108	1.4748–62	15° C
Croton.....	53–56	0.9500	15° C	210–225	102–104	1.4768	27° C
Rape.....	33–43	0.9132–68	15.5° C	170–179	94–102	1.4720–57	15° C
Castor.....	46–53	0.9600–79	15.5° C	183–186	83–86	1.4799	15° C

Soja Bean Oil. This oil is also known as soy bean and soja oil. It is obtained from the seeds of several varieties of the *Soja hispida* (glycine soja and soja max.), a plant growing in China, Manchuria and Japan. The whole fruit consists of a hairy pod, containing small round, yellow seeds, slightly smaller than the ordinary pea. Green and black varieties also exist. The seed or bean contains 16–19 per cent of oil and the commercial yield is about 13 per cent. The raw oil is deep brown in color and is not much improved by alkali treatment except when bleached. The odor and flavor are slight and not unpleasant, but the keeping qualities of the oil are not particularly good, and on storage a nauseous taste is likely to develop after a time. The oil is employed for edible purposes, although in a limited way. It is used in soap making, and has been tried as a paint oil, but its "greasy" properties have not led to extensive use in this field. Soja oil hydrogenates readily, forming a hard fat. The hydrogenation of this oil is extensively practiced.

Pumpkin Seed Oil. In South Russia the seeds of the *Cucurbito pepo* are roasted, and the oil expressed in the hot condition. This produces a viscous product of a deep red color. The cold pressed oil has a greenish color and a slight red fluorescence. The cold pressed oil is used for edible purposes, while the inferior grades serve as burning oils.

Corn Oil. This oil is obtained from the germ of the maize plant, *Zea mays*, during the manufacture of corn starch. The freshly prepared oil has a pale yellow color, and may be readily identified by its taste, which is similar to that of corn meal.

The keeping qualities of the oil are very good when refined, but the crude oil is rapidly hydrolized if meal be present. By careful refining and deodorizing with superheated steam, an edible product is obtained which has a very pleasant taste and whose keeping qualities are good. This grade of oil is used in cake and biscuit making and for oiling baker's pans, also in margarine and as a salad oil. Hydrogenated corn oil serves as a satisfactory stiffening ingredient in lard compound. Although somewhat difficult to saponify corn oil is used quite extensively in soap making and to a more limited degree in the manufacture of paint. The output of corn oil is, however, almost insignificant in comparison to that of cotton seed oil.

Cotton Seed Oil. This oil is obtained from the seed of the cotton plant (*Gossypium herbaceum* and other species of gossypium), extensively cultivated in the United States, Egypt, East India, and other countries. The oil as it comes from the hydraulic press varies in color from yellowish brown to a dark ruby or blackish red, depending on the nature and condition of the seed from which the oil has been expressed. It contains mucilage, fine meal or "mealy matter," coloring and tarry material. Some of these impurities are due to the effect of moisture and heat in pressing the oil from the cooked seed. Crude oils containing under 1 per cent of free fatty acid and derived from selected

seed are used in the manufacture of butter oils. Great care has to be taken in the preparation of butter oils to preclude the development of any unpleasant taste or odor. When about 1 or 2 per cent of fatty acid is present in the crude oil, refining is carried out to produce what is known as prime yellow oil. Above 2 per cent of fatty acids, there is more difficulty in removing the color, and the oil is not as suitable for edible purposes. Crude oil may contain as high as 7 or 8 per cent of free fatty acids in case the seed has become damaged by heating, etc. The losses occurring in the refining of the crude oil varies with the proportion of free fatty acids and usually runs from 7 to 10 per cent. Improved methods in refining are tending to reduce this loss.

Refining of Cotton Seed Oil. While the procedure of refining varies considerably with different operators, in general the method consists in adding to the oil a quantity of a solution of caustic soda, sufficient to combine with the free fatty acid to form a soap. The latter in separating from the oil occludes and drags down much of the foreign matter, leaving the oil much lighter in color and substantially free from fatty acids.

The soap also carries with it a certain amount of the neutral oil, and this mixture of soap, oil and coloring matter, etc., is called soap stock. It settles to the bottom of the refining kettle and is drawn off to be worked up into soap or fatty acids. The refining kettle is equipped with a mechanical agitator or a coil through which compressed air may be admitted to the bottom of the kettle so as to stir the oil vigorously when the alkali is added. When the lye is being added to the oil, the operation is closely watched to ascertain when sufficient alkali has been introduced. An initial temperature of 85–95° F. is maintained during the period of addition of alkali. A few minutes after the introduction of the caustic solution the appearance of the oil changes. The oil becomes more fluid, and turns to a brownish or black shade in the course of 15 or 20 minutes. When a sample shows a clear bright oil carrying blackish flock, it has reached the stage of " breaking," and the caustic soda supply is shut off. The oil is now heated with gentle agitation to a temperature of about 100–120° F. or so and the flocks or clots collect so that the oil will settle clear. The time required for the refining operation is approximately 30 to 45 minutes.

The clear oil is drawn from the refining kettle into a finishing or settling tank. In some cases the oil is washed with water to remove traces of alkali. With oils of medium quality this usually is not done, and it suffices to add a small amount of fuller's earth to absorb moisture and brighten the oil and to then pump it through a filter press when it goes to the storage tanks.

Fig. 287 shows the arrangement of refining apparatus, L being the lye tank, R the refining kettle, S the settling tank and F the foots or soapstock tank.

The refined oil may be bleached as described under the bleaching of oils with fuller's earth. Chemical bleaches likewise may be used, but

these usually impair the flavor of the oil and are not generally looked upon with favor by manufacturers of edible oils. Sometimes the crop of seed is so poor that fuller's earth proves ineffective as a bleaching agent and has to be supplemented by a chemical bleach. Treatment with chloride of lime and mineral acid, followed by thorough washing, affords a bleached oil which satisfies many industrial requirements. In some refineries carbon black is used to remove the red coloring agents from oil which does not bleach readily with fuller's earth. Chlorophyll in small quantity is sometimes added to improve the color. To obtain a

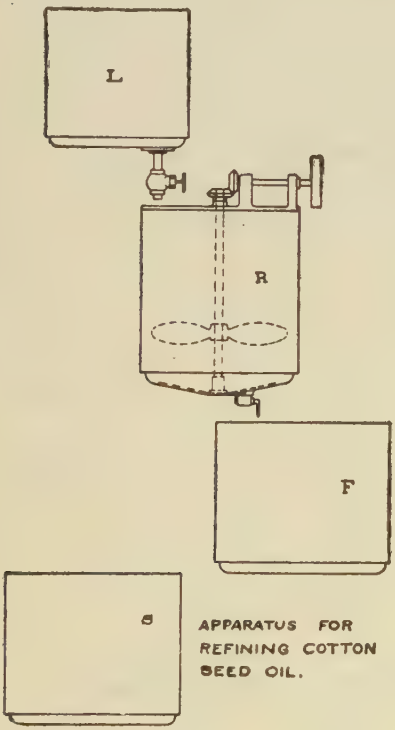


FIG. 287.

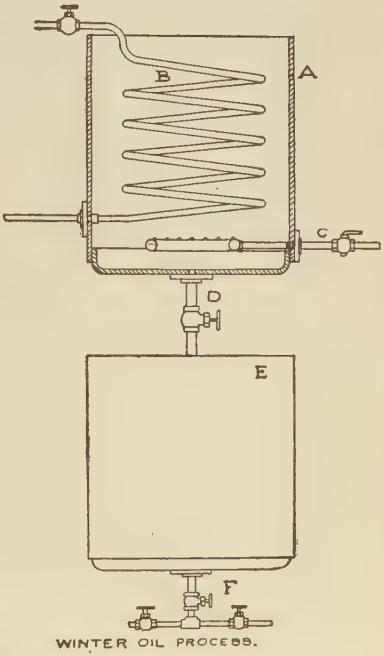


FIG. 288.

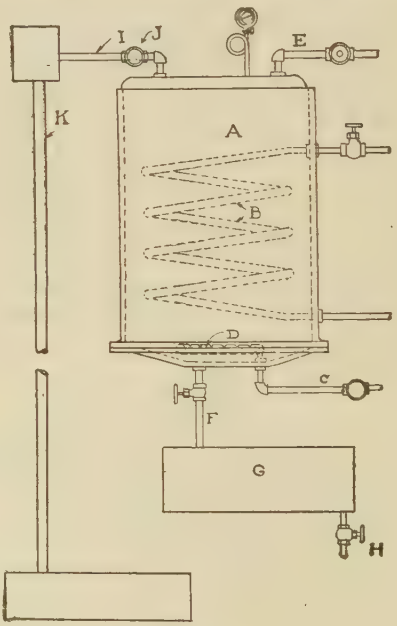
"red" oil for margarine manufacture affording the desired shade of yellow to the finished margarine, without use of dyes, the oil is treated with sulphur, or nitric oxide.

The market brands "summer oil" and "winter oil" differ from each other in that the latter has most of the stearine removed; so that the oil does not solidify during the colder months. Winter oil is sometimes spoken of as "demargarinated." The "cotton seed stearine" is of a light yellow color of the consistency of butter. It is manufactured on a very extensive scale in this country by cooling the oil, filtering off the solid deposit and pressing.

Apparatus for making winter oil is shown diagrammatically in Fig.

288. An insulated tank *A* contains a series of cooling coils indicated by *B*. In the lower part of the tank is an air pipe *C*. *D* is a draw-off communicating with a distributing tank *E*. The outlet *F* at the bottom of the latter tank serves to distribute the chilled oil to filter presses where the stearine is removed. The operation of making high grade winter oil calls for great care and watchfulness. In brief, the procedure consists in chilling the summer oil in the tank *A* while taking temperature observations at regular intervals. Analogous to the titer test, control may be had by ascertaining the fall and subsequent rise in temperature which occurs during the operation. At first the temperature falls until stearine commences to separate, then a rise occurs due to such separation. At intervals air is blown through the oil to agitate it thoroughly. Finally when the thermometer remains stationary for a sufficient interval the chilling stage is ended and the oil is discharged into the distributing tank *E* and is passed onward to filter presses where the stearine is removed and winter oil collected. In some plants it is the practice to expose the oil in tanks placed in a refrigerator room, but this is not as economical a method as the foregoing.

Deodorizing Cotton Seed Oil. The better grades of edible oil require deodorization, which is usually effected by subjecting the well refined oil to the action of superheated steam under reduced atmospheric pressure. An apparatus for carrying out this operation is shown in Fig. 289.



DEODORIZING OILS.

Fig. 289.

A is a deodorizing tank having the heating coils *B* and a steam inlet *C* terminating in the distributer *D*. *E* is a pipe for the admission of oil and *F* is a draw-off pipe for the deodorized product. *G* is a cooler for quickly reducing the temperature of the finished deodorized product. A vacuum is secured by the water leg *K* which is of sufficient height to "pull" a vacuum of about 20 inches mercury. In place of the water leg a pump may be employed to secure the reduction in pressure. The higher the vacuum produced the better the result and in fact more dependence is usually placed on high vacuum than on the effect of the superheated steam. A charge of oil is heated in the tank *A* to a temperature of say, 400° F., the temperature varying more or

less according to the nature of the oil. Superheated steam is passed through the oil at such a rate that the vacuum gauge indicates a degree of exhaustion of 20 inches or more.

When the oil has been sufficiently freed from odoriferous constituents it is withdrawn through the cooler *G* and discharged from the outlet *H* into storage tanks. Sometimes two deodorizing tanks are coupled in such a manner that they may be operated in series which enables a saving in steam to be made. The deodorizing operation also has been carried out as a continuous process. Before the withdrawal of the oil from the tank *A* the valve *J* should be closed and not opened until a fresh charge of oil has been introduced. It is desirable to keep air from entering the tank, because any residual oil therein would quickly become rancid and render frequent cleaning of the apparatus necessary. Also it is desirable to quickly cool the oil after its withdrawal from the deodorizer in order that the flavor may not be impaired.

Cotton seed oil is used in large quantities for edible purposes, but owing to popular prejudice in the past it has seldom appeared under its true name. Of late, this prejudice has greatly diminished. We may find it on the open market as "table oil," "salad oil," "sweet nut oil" as well as a score or other designations. Large quantities of the cotton seed stearine are employed in the manufacture of "oleomargarine," butter compounds, butter substitutes, lard compounds, and lard substitutes. Cotton seed oil being cheap is often used as an adulterant for the more expensive oils such as olive, peanut and other edible oils. One of its most important uses is in the manufacture of toilet and laundry soaps.

Sesame Oil. This oil is obtained from *Sesamum orientale,* extensively grown in India, China, Japan, the Levant, and West Africa. The cold pressed oil is of a light yellow color, with a pleasant taste, so that it is used to some extent for edible purposes. In some countries the legal requirement is made that sesame oil form a constituent of margarine in order to facilitate the detection of margarine in butter. The hot pressed oil is used largely in soap making.

Croton Oil. Croton oil is obtained from the seeds of *Croton tiglum,* a tree grown on the Malabou Coast, in Southern Asia, and in China. The oil varies in color from yellow, orange, or brown according to age. It has a nauseating odor, a burning taste, and a very powerful purgative action. Its chief use is in pharmaceutical preparations.

Rape Oil. There are several varieties of this oil, depending upon the place of cultivation. The oil is obtained from the seeds of *Brassica campestris.*

In the trade this oil is called colza oil. The crude oil is dark brown and may contain a considerable proportion of free fatty acids. The refined oil is pale yellow and is very viscous, depositing more or less stearine on standing. The taste is unpleasant and the odor characteristic. Refined cold drawn oil is sometimes used for edible purposes, while the inferior qualities find an outlet as lubricants and illuminants. Rape

oil as well as cotton and corn oil are converted into rubber substitutes or factis by treatment with sulphur chloride or by heating with sulphur. Rape oil also is "blown" with air to produce thickened products.

Castor Oil. This oil is obtained from the seeds of *Ricinus communis*, a plant grown extensively in East India, Java, the Mediterranean countries, and the United States. The cold pressed oil is used for medicinal purposes. The lower grades are used very extensively in manufacturing operations, such as leather dressings, and in the sulphonated condition is known as "soluble oil" "Turkey red oil" or "monopol oil." Castor oil is a colorless or pale greenish oil with a mild taste.

It has a high viscosity and finds some application in lubricants, although by no means devoid of gumming properties. The oil is prized as a lubricant for aeroplane engines. Sulphur unites readily when heated with it forming rubber-like compounds. When hydrogenated at a relatively low temperature, the hydroxyl groups present are not affected, but at higher temperatures these are replaced by hydrogen. The hydrogenated product is very hard and has found a use in the manufacture of insulating materials. A peculiar property of castor oil is its miscibility with alcohol. Unlike most other oils it does not dissolve readily in petroleum ether. By heating to a rather high temperature the oil becomes polymerized and is then miscible with petroleum ether and mineral oils.

Vegetable Non-drying Oils. The oils in this class have a lower iodine number than those of the two preceding classes. They do not become gummy when exposed to the air at ordinary temperature; although they all thicken on heating.

Name of Oil.	Oil Content of Seed, Per Cent.	Specific Gravity.		Saponification Value.	Iodine Value.	Refractive Index.	
Peach kernel	32–35	0.918 0.9215	15° C	191.5	93.3– 100.3	1.4713	15° C
Almond	45–55	0.9175 0.9195	15° C	199.3	100.7	1.4731	15.5° C
Peanut	43–45	0.9170– 0.9209	15° C	191.3	94.7	1.4766	15.5° C
Olive	40–60	0.916–18	15° C	185–196	79–88	1.4698– 1.4716	15° C
Olive kernel	12–15	0.9184– 0.9191	15° C	183	87.4	1.4682	25° C

Peach Kernel Oil. This oil is obtained from the kernel of the peach, is of a pale yellow color, and greatly resembles almond oil. Its chief use is as an adulterant for almond oil.

Almond Oil. Almond oil is expressed from bitter almonds, which yield more oil than sweet almonds, although both oils are practically identical. The source of this oil is Morocco, Canary Islands, Portugal,

Spain, France, Italy, Sicily, Syria, and Persia. Its chief use is in pharmaceutical preparations.

Peanut Oil. This product is also known as earthnut oil and arachis oil. It is obtained from the seeds of *Arachis hypogaea*, commonly known as peanut. It is largely cultivated on the West Coast of Africa, India, and the United States. The nuts are shelled and the inner red skin separated as completely as possible from the true kernel. The kernels are then pressed. The oil has a golden yellow color and the edible varieties are usually bleached to a very pale color. The cold-pressed oil is nearly colorless, has a pleasant flavor and is largely used as a salad oil. The inferior qualities are used in soap making.

Olive Oil. The oil is prepared from the fruit of the olive tree, both by expression and extraction. The commercial product varies from colorless to golden yellow and dark green, according to the variety of tree, degree of ripeness, manner of gathering, and method of expression. "Virgin oil," considered the best quality for edible purposes, is obtained from the hand-picked fruit, by crushing in such a manner as not to break the kernel. The pulp is then treated with water and pressed again. By this process salad oils are obtained. The pulp is then removed from the press, treated with hot water and again subjected to hydraulic pressure; the oil obtained being employed for lubricating, soap making, and for other technical purposes. The final expression comes into the market as " olive oil foots," extensively employed in the manufacture of " castile " soap.

The best quality of the oil is greenish yellow. The consistency is that of a limpid oil at ordinary temperatures and beginning to deposit " stearin " below 10° C. The oil is valued more particularly on its flavor. The finest edible oil has practically no smell and very little taste, but with inferior grades there is a distinct odor and the taste becomes sharp and unpleasant, due in part to increasing proportions of free fatty acids. The best edible oil contains only 0.3–0.5 per cent of free fatty acids, and anything much exceeding this precludes its use as a salad oil. The acidity is sometimes removed by treatment with alkali, and oils treated in this way do not show the absorption bands of chlorophyll which are often clearly given by the fresh oil.

Olive Kernel Oil. This oil is obtained by pressing or extracting the seeds from olive stones. The cold-pressed oil is golden yellow in color, while the hot-pressed oil has a greenish cast. The extracted oil is dark green in color, probably due to the presence of chlorophyll. This oil in a way is the by-product in the manufacture of olive oil, and resembles it very closely in all of its properties.

Animal Oils. These oils are obtained by heating the fatty matter with live or dry steam in open kettles or closed digesters; the old method of heating over the open fire is now used but infrequently. One of the most modern processes consists in heating the stock with water, at a pressure sufficiently high to cause a complete separation, but not high enough

to decompose the stock. When this " rendering " is complete the contents of the digester is filtered to remove solid matter, and the liquid portion allowed to stand so that the oil may rise to the top. The liquid portion remaining after the oil has been removed, may be used again, or may be concentrated for use as glue stock. The solid matter is usually dried and sold for use in fertilizers. In some forms of rendering tanks the oil is allowed to rise to the top, where it is removed by tap valves along the side. The oil obtained by the above methods is usually sufficiently pure for commercial purposes. If it is to be used for edible purposes, it is customary to further purify it by bleaching. This is accomplished by passing the oil or fat through bone-black or fuller's earth.

Animal oils may be divided into two classes;

1. Marine animal oils, 2. Terrestrial animal oils.

Marine Animal Oils. The marine animal oils are characterized by their high iodine values, which in a way resemble the vegetable drying oils. As with vegetable oils, we have a gradual lowering of the iodine value through drying, semi-drying, and non-drying oils, until we approach the constitution of the terrestrial animal oils. The members of this class of oils are liquids at the ordinary temperature, and will be considered under the three following groups:

Fish oils Liver oils Blubber oils

Fish Oils. The fish oils are obtained from various parts of the body of such fish as menhaden, herring, sardine, salmon, etc. The fish, or oily portion, is placed in rendering tanks, boiled and the oil drawn off from the top. The soluble portion is used for making fish glue, isinglass, and the solid portion sold as a fertilizer under the name of fish scrap.

TABLE OF CONSTANTS FOR SOME COMMON FISH OILS

Name of Oil.	Specific Gravity.		Saponification Value.	Iodine Value.	Refractive Index.	
Menhaden.....	0.927–0.933	15.5°C	190.6	139–180	1.480	15°C
Sardine.....	0.933	15 °C	.....	161–193	1.479	15°C
Salmon.....	0.9258	15.5°C	182.8	161.4	.....	.....

Menhaden Oil. This oil is prepared from the body of the fish, which in appearance resembles herring, although it is somewhat larger. The time of fishing for menhaden is determined, of course, by the habits of the fish. Since they appear in northern waters in April and disappear in November, the fishing season is limited by those months. As one goes farther south, the season is lengthened; in the Carolinas the boats are not put out of commission until the latter part of December, though

fishing does not begin much earlier there than in the northern regions. In the southern region, the spring and fall fishing furnishes most of the raw material, there being a dull season in mid-summer when catches are rare and unimportant. In Florida waters the fish are present throughout the winter. To illustrate some of the methods employed in rendering oils of this character the following detailed description is given:

Cooking. (Old Method.) The old method of cooking in open vats is still in vogue in such a number of factories as to justify its description here. The vats employed are usually situated on the second floor of the factory so that the mixture of oil and water subsequently to be pressed from the cooked fish can follow its prescribed course through the plant without the assistance of pumps. They are constructed of wood or cement, with a false bottom, beneath which are placed steam pipes. The individual vats may have a capacity of about 20,000 fish, and the entire set of vats, 300,000 fish. They are arranged generally in two adjacent longitudinal rows. Above them runs the truck conveying the tram cars or the automatic conveyor which supplies the fish to be cooked, while along either side of the double row are placed other tracks running to the presses.

Fish are dumped into the vats in quantities depending on the capacity of the vats, usually 50 to 100 barrels, some water is added and the steam is turned on. They are cooked about 20 minutes, or a sufficient length of time to cause them to break up easily, but not long enough to disintegrate them entirely. The object of the cooking is to break the oil cells or to bring about that condition which admits of a more ready expressment of the oil. If the cooking is too prolonged this is accomplished also, but the flesh is so thoroughly disintegrated that it becomes a mush from which it is difficult to separate the oil: the oil, water, and fine particles of flesh would then squeeze out of the presses together.

Pressing. (Old Method.) The cooked fish are thrown from the vats into the curbs of the presses by means of a modified shovel which retains the solid matter and permits the water to run back into the vats. The escaping water and oil is caught by the properly slanting floor as is also that escaping from the curb during charging, and conveyed to the oil room for settling and further treatment. When the maximum pressure has been applied and no more liquid is being forced out, the pressure is released and the curb is rolled over an opening in the floor for emptying. The bottom is then released and swings downward, and the mass of fish scrap falls in a solid cake to the floor below. The slanting sides of the curb are designed to facilitate the discharge of this cake; the curb being larger at the bottom than at the top, the cake falls out more readily. At this stage, the scrap contains about 50 per cent water, by weight, and about 6 or 9 per cent of oil.

Cooking. (New Method.) The new method of cooking fish largely has supplanted the old because of its speed and efficiency and the saving

in labor which it effects. The apparatus employed is essentially a long, narrow, iron cylinder, of varying lengths, but frequently about 40 feet, and about 2 feet in diameter, through which the fish are passed by means of a screw conveyor, being subjected the while to the cooking action of steam. There are several forms of this apparatus, differing from each other principally in the manner in which the steam is admitted to the cylinder. Thus, it may be admitted through perforations in the hollow shaft of the screw conveyor; the blades of the conveyor may be substituted for by sections of iron pipe, arranged screw-wise around the axis, through perforations in which the steam may enter the chamber; or it may be admitted through numerous pipes projecting from the outside through the casing along its bottom.

The second and third methods mentioned are regarded by the operators as more efficacious, as they admit the steam within the mass of fish, instead of above it, and thus effect more thorough and uniform cooking. The fish are conveyed automatically from the storage bins and are dumped continuously into the hopper-like mouth of the cooker. This, in certain forms, is provided with a special device for regulating and assisting the feeding. The cooked fish, together with the water and oil cooked from them and the water resulting from the condensed steam, are passed from the end of the cooker into the buckets of a conveyor and are transported to the presses.

Pressing. (New Method.) The modern power press employed in fish scrap industry partakes of the shape of a truncated cone placed in a horizontal position. It is essentially, a curb, constructed of iron, with slatted sides. Through its center passes a horizontal shaft on which is built up a screw, tapered to fit closely inside the cone-shaped curb. The rotation of the screw carries the fish forward into the smaller end of the curb; and as the material cannot rotate with the screw, or slip on the curb, it is subjected to pressure. By adjusting the size of the opening in the smaller end, through which the expressed material is ejected, the pressure on the mass may be increased or decreased. The pressure is gradual, increasing from the larger and toward the smaller. The water and oil are squeezed out between the slats and are caught by the metal shield surrounding the press and are conducted thence into pipes leading to the oil room. The mouth of the press is hopper-shaped. The fish are fed into this by a mechanical conveyor. In some forms of the press, a chopper is placed in the mouth to reduce the size of the pieces of fish entering. From the smaller end of the press the fish scrap usually is allowed to fall into the buckets of a conveyor.

One hundred pounds of the mass coming from the cookers contain 22 pounds of fish solids and 78 pounds of water. In the press, 56 pounds is removed. This leaves a mass of 44 pounds of which about one half is water.

The press cake is dried usually in hot air driers which are iron cylinders

about 6 feet in diameter and about 30 or 40 feet in length. On the inside are a series of iron flanges or shelves about 8 inches wide and running the length of the cylinder. These are designed to lift the scrap and charge it through a stream of hot air. The drier is slightly inclined and is rotatable so the wet fish scrap when charged at the upper end moves along the barrel of the drier and is discharged at the lower end. The heating furnace is arranged at the upper end, hence the hot gases travel in the same direction as the scrap and the forced draft which is employed serves also to blow the scrap through the kiln.

Menhaden oil, the true fish oil, is by far the most important oil produced on the Atlantic Coast of the United States. The annual production exceeds two million gallons.

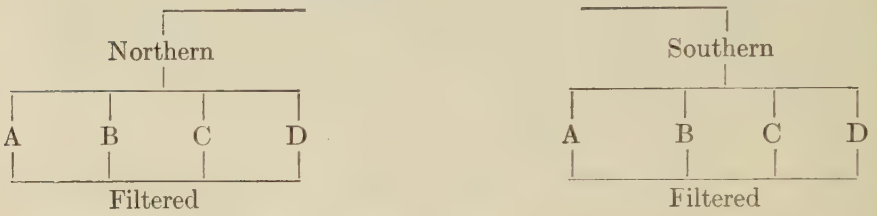
Technology. The mixture of oil and water running from the cooked fish in the presses is conducted into the first and uppermost of a set of tanks, arranged one somewhat above the other. In this vat the mixture on standing a short time separates into a stratum of oil floating on an aqueous layer. The separation may be assisted by heating the mixture. For this purpose steam coils are provided. The oil is allowed to flow thence by a suitable arrangement of weirs successively through the series of receptacles, in which by means of stronger heating by steam it is gradually purified from its contained water and small particles of flesh. The greater part of the fine particles of flesh separate in the first vat, settling to the bottom. This fine mush is known as "gurry," and sometimes is sold to the manufacturers of soap without further treatment, and in some cases is placed in stout canvas bags and subjected to pressure to recover the oil which it still contains. The residual solid matter is added to the scrap. As this is free from bones, its nitrogen content is correspondingly higher that that of the ordinary scrap.

Yield. The yield in oil varies (1) with the year, (2) more decidedly with the locality from which the fish are taken, and (3) most widely with the time of the year when taken. The fish taken in northern waters as a rule are fatter than those from southern waters. "In the year 1900, for instance, the yield of oil at the Rhode Island factories was 5.76 gallons per 1000 fish; in New York it was 6.39 gallons; in Delaware 4.92 gallons; and in Texas 3.51 gallons to the 1000 fish." When the fish appear in the spring they frequently are so thin that no recoverable oil at all is obtained from them. The fish taken in the fall, on the contrary, yield on the average 12 gallons per 1000 and frequently 15 gallons per 1000. The variation in average yield per thousand from year to year, therefore, probably is determined by the relative number of fish caught in the spring and fall.

Properties and Uses. Crude menhaden oil varies in color from light amber to dark brown. The oil comes into the market as "prime crude," "brown strained," "strained," "bleached winter oil" and "bleached winter white oil." Grade is also indicated by letter and the grading

is carried out simply by color observation. The classification is indicated by the following table:

MENHADEN OIL



The northern oil is regarded as slightly better than the southern oil for the reason that it is presumed less decomposition of the fish is likely to take place prior to expressing the oil when the catch is handled in cooler climates. There is a great variation of the iodine number, the maximum being about 180.

Standard samples of crude northern menhaden oil show a glycerine value of slightly over 10 per cent and an iodine number of 175. Crude southern menhaden shows a glycerine value of about 10 and an iodine number of 168. Filtered northern menhaden shows a glycerine value of about 10.2 and an iodine number of 166 and is obtained by cold pressing. Filtered southern menhaden shows a glycerine content of about 9.9. and an iodine number of 167. The specific gravity ranges from about 0.927 to 0.933.

Crude menhaden oil runs from 3 per cent and upwards in fatty acids. The filtered oil is usually bleached. The southern oil is popularly supposed to be of a lower iodine value and not so good a paint oil as the northern product. The southern oil is apt to be higher in free fatty acid due to its being obtained in a hotter climate.

Formerly menhaden oil was used principally as an illuminant and in currying leather. In addition, it has long been used as a paint vehicle, as a lubricant and as a soap-making grease. Its use in currying leather and as an illuminant has been supplanted to a considerable extent by that of mineral oils, while its employment in the other manners mentioned has increased. Large and increased quantities are now used in the paint manufacturing industry, and in tempering steel. For the latter purpose a large amount is sold directly to the manufacturers of steel articles. Menhaden oil also is used in linoleum or oilcloth manufacture and for making hardened oil by hydrogenation. The lower grades of fish oil are somewhat difficult to hydrogenate owing to the impurities present which poison the catalyzer. The better grades of oil may be hardened to products of excellent quality suitable as substitutes for tallow in soap making.

For paint making bleached oil usually is not regarded as desirable,

Bleaching is thought to some extent to effect the oil for paint making purposes. For exterior work, 3 parts of fish oil may be used with one part of linseed oil. Fish oil is more resistant to the action of heat than linseed oil and hence is especially adapted for use in painting iron work, such as boiler fronts and smoke stacks. Its use is recommended especially for replacing linseed oil in the manufacture of patent leather and similar products, and printing ink. The patent leather resulting is more flexible and less liable to crack though it possesses a somewhat less glossy surface. An objection to its use in this manner, however, is a peculiar efflorescence which its presence causes to form on the surface of the preparation. Its moderate use in the manufacture of baked japans also has been found highly advantageous.

Sardine Oil. This oil is obtained in the preparation of canned sardines. It is also made on a large scale in Japan by chopping the fish and subjecting them to boiling and pressing.

Salmon Oil. This oil is obtained on a large scale as a by-product in the canning industry of British Columbia. It is of a pale golden yellow color, with very little odor, and not unpleasant taste.

Liver Oils. As the name implies, these oils are obtained from the liver of various species of fish. They form a natural group which is characterized by the large amount of cholesterol, and biliary substances present in them. The iodine values bring them between the fish and blubber oils.

CONSTANTS FOR LIVER OILS

Name of Oil.	Specific Gravity.		Saponification Value.	Iodine Value.	Refractive Index.	
Cod liver.....	0.9210–70	15°C	171–189	167	1.4800–52	15°C
Haddock liver.....	0.9298	15°C	188.8	154.2	.....	.....
Shark liver.....	0.9163	15°C	161	114.6	.....	.....

Cod Liver Oil. There are many grades of cod liver oil on the market, obtained in various ways from the liver of the cod fish. The purest form of oil for medicinal purposes is that prepared from fish which are brought ashore alive. The livers are heated in jacketed kettles, the resulting oil being known as "steamed liver oil." When it is impossible to bring in the live fish, they are opened and the livers collected. Provided no decomposition has taken place the oil obtained from this stock is known as "pale cod liver oil" and is used to some extent for pharmaceutical purposes. As often happens these livers are landed in a more or less putrid condition, so that the oil from them becomes unfit for medicinal use, and is known as "light brown oil." Should the product become very putrid the resulting oil is known as "brown oil." The oil not suitable for medicinal purposes is used in the currying of leather under the name of "cod oil."

What is known as dark tank cod oil comes from Newfoundland and has a specific gravity of .9296; an iodine number of 129; fatty acid content 14 per cent and saponification number 190. Dark tank cod oil is made from cod livers and is used for tanning.

Cod liver oil contains quite an amount of stearine which, to a great extent, settles out on standing. Oils which have been freed from stearine are known as "raked" oils.

Shark Liver Oil. This oil is used to some extent as an adulterant of cod liver oil; it is obtained in a manner very similar to that employed for cod oil. It is also used in the leather industry. The oil appears on the market as "yellow strained," "red," "yellow," "yellow red," "Japanese," "crude," and "refined."

Haddock Liver Oil. The oil from haddock liver closely resembles cod liver oil, to which it is added to quite an extent as an adulterant.

Dog-fish Liver Oil is an ill-smelling "fishy" oil which requires energetic refining to yield an acceptable product.

Blubber Oils. Under this heading will be included those oils obtained from the blubber of various fish. They differ from each other quite widely in their chemical composition.

CONSTANTS OF SOME BLUBBER OILS

Name of Oil.	Specific Gravity.		Saponification Value.	Iodine Value.
Seal	0.9155–63	15°C	189–196	127–145
Whale	0.9180 to 0.9300	15.5°C	188	115–155
Dolphin	0.9180	15°C	197.3	99.5
Porpoise	0.9258	15°C	195	

Seal Oil. This oil is obtained from the blubber of the seal. It varies in quality depending upon the method of extraction, and the length of time the oil has been left in contact with the animal tissue. The following brands appear on the market: "water white," "straw seal," "yellow seal," "and brown seal." The last named oil is the result of long contact with animal matter and extraction at high temperatures.

A white steam refined oil is produced only during the month of May in Newfoundland. It resembles whale oil but is not as "fishy." Its principal use is as a soap oil. Analytically seal oil resembles whale oil.

Whale Oil. Formerly the whale blubber was worked up on board the whaler, but now it is generally brought into the "trying" station. The blubber is stripped from the flesh as completely as possible immediately when it arrives at the works. It is cut into strips, delivered to the melting pan, and boiled with steam. The best quality of the oil is of a very pale

yellow color, and is known in the trade as " whale oil No. 0." The fishy odor is relatively very slight. On further heating the next quality, " whale oil No. 1," is obtained, which is a little darker in color, and has more of a fishy odor than No. 0. Bleached No. 1 oil is sometimes sold as No. 0. The residue in the pan, together with the flesh of the whale, is heated in a digester under pressure of about 50 lbs. to the square inch. In this way " whale oil No. 2 " is obtained, which is of a brown color, and strong fishy odor. When the bones are worked up an oil is obtained known as " whale oil No. 3." This oil is darker than No. 2 and has a very strong odor. From the flesh which has undergone putrefaction " whale oil No. 4 " is obtained, this is still darker in color and has a very objectionable odor.

Nos. 2, 3 and 4 are graded by color.

No. 1 is pale yellow. No. 2 is orange. No. 3 oil in the crude state may be likened to coffee containing cream. No. 4 oil is practically a black oil.

About 60 per cent of the total oil from whale is the No. 1 grade. Thirty per cent is the No. 2 grade and the remainder is Nos. 3 and 4. No. 0 does not appear on the market in material quantities. In this country No. 1 whale oil is frequently sold with an acid guarantee of not over 2 per cent. The No. 2 oil should not contain more than about 5 per cent free fatty acid. No. 3 will run up to 15 per cent or so of fatty acid. During the last few years, there has been an increasing tendency to make the free fatty acid test a basis of contracts. As a matter of experience, it has been found that an oil which falls below the highest figure representing the limit of free fatty acid for a particular grade, will also conform to the accepted color standard for that grade. There are exceptions, as, for instance, when an oil is discolored by iron compounds. The specific gravity of fish and whale oils ranges from .918 to .930. The iodine number of crude whale oil is very variable and ranges between 115 and 155 for all classes of these oils.

In the pressing of whale oil to secure products of the proper cold test, a quantity of so-called stearine is obtained which is used mainly in the preparation of whale oil soap and for making railway coach lubricants.

No. 1 filtered whale oil has a flash point 570° F. and burning point 640° F. The viscosity at 100° F. is 166 seconds in the Saybolt instrument. No. 3 filtered whale oil has a flash point of about 380° F. and burning point of 424° F.

The maximum production of whale oil is about 60,000 barrels annually, this being obtained mostly in Canada especially along the Canadian Pacific Coast. Only a small proportion comes from the American Pacific coast. A very small and uncertain supply is derived from the Eastern coast, but the whaling industry which formerly made New Bedford an important port no longer exists and the industry is at its height now along the Canadian Pacific shores.

A small amount of sea elephant oil is brought into this country, but is usually sold as whale oil.

The uses of whale oil are confined largely to the following:

For hydrogenation purposes to produce edible products and fats suitable for soap making; for tempering. It is not used in tanning to any great extent in this country although it has found favor for this purpose elsewhere. Hydrogenated Norwegian oil is a clean product of unusually high quality. The water white and pale brands of whale oil are used for burning, and for soap making, the brown quality being used for leather dressings.

Dolphin Oil. The oil obtained from the blubber of the black fish, in its chemical composition, is intermediate between whale oil, a glyceride, and sperm oil, a wax. There are two varieties of this oil, body oil and jaw oil. Both are of a pale yellow color, and contain large amounts of glycerides of volatile fatty acids. On standing spermaceti deposits. It is used for lubricating fine machinery; such as watches, and other delicate instruments.

Porpoise Oil. This oil is obtained by boiling the entire tissue of the brown porpoise; it is of a pale yellow color, and consists of the glycerides of valeric, palmitic, stearic, and oleic acids. There are two varieties of the oil, body oil, and jaw oil. It is used as a lubricant for delicate machines.

Terrestrial Animal Oils. The oils of this class have a low iodine number, and therefore, belong to the non-drying oils.

CONSTANTS FOR TERRESTRIAL ANIMAL OILS

Name of Oil.	Specific Gravity.		Saponification Value.	Iodine Value.	Refractive Index.	
Sheep's foot...	0.9175	15° C	194.7	74.2		
Horse's foot...	0.913–27	15° C	195.9	73.8–90		
Neat's foot....	0.914–16	15° C	194.3	69.3–70.4		
Egg.....	0.9144	15° C	184.4–190.2	68.5–81.6	1.4713	25° C
Lard oil.....	0.916	15° C	193	73		
Tallow oil.....	0.794	100° C	.....	55.8–56.7		

Sheep's Foot Oil. This oil is obtained from the feet of sheep in very much the same manner as described for neat's foot oil, it being similar to neat's foot oil, and is usually sold as such.

Horse's Foot Oil. As a rule this oil is never placed on the market under its true name, but is usually mixed with sheep's foot, or neat's foot oil. What is sold as horse oil is the liquid portion of horse fat. The odor is rarely of a pleasant character.

Neat's Foot Oil. This oil is obtained by boiling the feet of cattle with water. It is of a pale yellow color and free from odor. The commercial product usually contains small amounts of sheep's foot and horses' foot

oils. On account of the high price of neat's foot oil it is often adulterated with vegetable, fish, or even mineral oils. The most common adulterants are rape oil, cotton seed oil, corn oil, menhaden or other fish oils, and mineral oil. True neat's foot oil is an excellent lubricating oil, but its chief application is in leather manufacture.

Egg Oil. This oil may be obtained by pressure or extraction from the hard boiled yolk of hen's eggs. The pressed oil has a yellow color, while the extracted oil is of an orange shade. The nature of the solvent largely influences the properties of the oil obtained; those most commonly used being ether and petroleum ether. In the form of egg-yolk it has very valuable properties in certain tanning operations.

Lard Oil. This oil is obtained by subjecting lard to hydraulic pressure. It consists in the main of olein with a small proportion of the glycerides of solid fatty acids, chiefly palmitic acid. The quality of the oil varies greatly according to the pressure and temperature maintained; hence, the constants will vary within a considerable range. Its principal use is as a lubricant, and in cutting oils.

Tallow Oil. This oil is the fluid portion which is separated on subjecting tallow to expression. The processes of manufacture and the properties of this oil are similar to lard oil. It also resembles neat's foot oil but contains a larger proportion of saturated glycerides and is regarded as less valuable as a lubricant.

Solid Fats

Vegetable Fats. To this class of fats belong those which remain solid at the ordinary temperature. They differ, however, very greatly in consistency, ranging from soft to very hard. This variation in hardness is dependent upon the amount of glycerides of oleic and linoleic acids present; the smaller the amount of these glycerides the harder the fat.

CONSTANTS FOR VEGETABLE FATS

Name of Fat.	Specific Gravity.		Saponification Value.	Iodine Value.	Refractive Index.	
Cotton seed stearine	0.9188–0.9230	15°C	195	90–103		
Palm oil	0.921–0.9245	15°C	192–202	51.5	1.4510	60°C
Vegetable tallow	0.918	15°C	200.3	28–37		
Cocoa butter	0.9500–0.976	15°C	193.5	32–41	1.4496	60°C
Palm kernel oil	0.9520	15°C	242–250	13–14	1.4431	60°C
Cocoanut oil	0.9115	40°C	246–260	8–9.5	1.4410	60°C
Japan wax	0.9700–0.9800	15°C	217–237.5	4.9–9.5		
Shea butter			180–190	57–63		

Cotton Seed Stearine. This product is manufactured on a very large scale by cooling cotton seed oil, and collecting the resulting solid which separates out. It is of a light golden color, of about the consistency of butter, for which it is used as an adulterant and it is also used in making margarine. It has also been employed as a lard substitute.

Palm Oil. Until recently, the only source of this oil was from the coast of Africa, but at present considerable quantities come from the Philippines. The oil is obtained from the fleshy part of the fruit of the palm tree. The process of making this oil is very crude. Either the fruit is stored in holes in the ground, when by fermentation the oil separates and rises to the top; or, the oil is pressed out by hand. The kernels are not destroyed, and from them palm nut oil is obtained. The fresh oil has a deep orange yellow tint not destroyed by saponification, a sweetish taste and an odor of orris root or violet which is also imparted to soap made from it. The methods by which the natives obtain the oil are crude and depend upon a fermentation or putrefaction. Large quantities are said to be wasted because of this fact. The oil contains impurities in the form of fermentable fibre and albuminous matter, and consequently develops free fatty acid rapidly. Samples tested for free acid have been found to have hydrolized completely and it is seldom one obtains an oil with low acid content. Because of this high percentage of free fatty acid, the glycerine yield is small, though the neutral oil should produce approximately 12 per cent of glycerine.

Since soap made from palm oil is colored orange, bleaching before saponification is usually required.

Oxidation readily destroys the coloring matter, while heat and light assist materially. The methods generally employed are by the use of oxygen developed by bichromates and mineral acid and direct bleaching through the agency of the oxygen of the air.

Bleaching of Palm Oil with Bichromate. The chrome process of bleaching palm oil is more rapid and the oxygen thus derived being more active will bleach oils which air alone is not able to decolorize. For the best results an oil should be chosen containing under 2 per cent impurities and a low percentage of free fatty acids. The grade of palm oil known as Lagos oil is best adapted to these requirements. The oil is melted and filtered to remove the fibrous material and gross impurities. The oil thus obtained contains fine earthy and fibrous material and albuminous matter which should be removed, as far as possible, since chemicals are wasted in their oxidation and the bleaching is retarded. This is best done by boiling the oil with wet steam and a 10 per cent solution of common salt. After settling over night the brine and impurities are removed and the oil is run into the bleaching tank. This tank is a lead-lined iron vessel of the approximate dimensions $4\times4\times4$ feet, having a content of about $1\frac{1}{2}$ tons. The charge is about one ton. The tank is equipped with a steam coil

and a coil arranged to allow thorough air agitation, both coils being of lead. These coils should extend over the bottom of the tank and have a number of small downward perforations. The temperature of the oil is reduced to 110° F. by passing in air, and 40 pounds of fine common salt per ton are added. About one-half of the acid (40 pounds of concentrate commercial hydrochloric acid) is now poured in and this is followed by the sodium bichromate in concentrated solution, previously prepared by dissolving 17 pounds of bichromate in 45 pounds commercial hydrochloric acid. This solution should be added slowly, the whole mass meanwhile being thoroughly agitated with air and for one hour after the last of the bleaching mixture has been introduced. The batch is allowed to settle and the exhausted chrome liquors are then run off. Water is run into the bleached oil and the temperature raised by open steam to 150° to 160° F. The mass is then allowed to settle.

Air Bleaching of Palm Oil. The method of conducting this process is identical with the chrome process to the point where the chemical bleaching agents are to be added to the oil. In this method these are unnecessary, as the active bleaching agent is the oxygen of the air. The equipment is similar to that above, except that a wooden tank in which no iron is exposed will suffice to contain the oil. The rapidity of the process depends upon the amount of air blown through the oil and its even distribution. Iron should not contact with the oil during bleaching, as it retards the process considerably. After the impurities have been removed, as outlined above, the temperature of the oil is raised by open steam. The steam is then shut off and air is allowed to blow through the oil until it is sufficiently bleached, the temperature being maintained above 150° F. by occasionally passing in steam. Usually the oil completely bleached after air has been passed through it for 18 to 20 hours, provided the oil is thoroughly agitated by a sufficient flow of air. When the oil has been bleached to the desired color, (which can be determined by removing a sample and cooling) the mass is allowed to settle, the water run off to a waste tank from which any entrained oil may be skimmed off and the supernatant clear oil run to storage tanks. While this process consumes more time, and is not as efficient in bleaching the lower grades of oils, the cost of bleaching is less and with a good oil success is more probable, as there are no chrome liquors present to contaminate the oil. These, if present, would give the bleached oil a green tint when the chrome method is improperly conducted. Instead of blowing the air through the heated oil the latter may be brought into contact with the air, either by a paddle wheel arrangement, or by pumping the oil into an elevated vessel, pierced with numerous fine holes from which the oil continuously flows back into the vessel from which it is being pumped.

Palm oil is much prized as a soap material and finds some use as a flux in the manufacture of tinned iron (sheet tin). It has been

proposed as an addition to oleomargarine to tint the latter a yellow color.

Vegetable Tallow. From the fruit of the Chinese tallow tree is obtained a hard fat. The fruit is steamed in perforated vessels, in which the fat melts and is run off. The remaining seeds are then pressed and "Stillingia oil" obtained. Another process is also employed in which the whole fruit is crushed and pressed, thus yielding a mixture of vegetable tallow and Stillingia oil.

Cocoa Butter. The cocoa beans are roasted, ground, treated with sodium carbonate and hot pressed. When freshly prepared cocoa butter has a yellowish color, but it turns white on standing. It has a pleasant odor and agreeable taste, and is less likely than almost any other fat to go rancid. It is used in confectionery, medicine, toilet creams, and soaps.

Palm Kernel Oil. This oil as indicated above, is obtained from the kernels of the palm tree fruit. After the fleshy part of the fruit is removed the kernels are collected, screened, ground to a pulp and subjected to hydraulic pressure. It is a white oil, and when fresh has a pleasant odor and nutty taste. It is used very largely for soap making, and in the pure condition it is employed for edible purposes.

"Stearin" from palm kernel oil is produced commercially of a somewhat higher melting point than that from cocoanut oil, and the "olein" may have a lower melting piont than that of cocoanut "olein." There has been a prevailing belief that the keeping properties of palm kernel products were not as good as those of cocoanut oil, but owing to improved methods of refining, this difference no longer exists.

Cocoanut Oil. The source of this oil is the fruit of the Cocos nucifera (The ordinary cocoanut tree). The husk of the nut is removed by hand. The nut is split in two and is dried in the sun, which requires two or three days. The shell comes off soon after the drying has commenced. The dried meat is termed copra. Large quantities of copra are prepared by drying in kilns, but the color is usually darker when so treated. The copra generally is shipped and pressed at a place near the point of consumption to avoid loss of oil by leakage in transit and to save the expense of containers. The oil is a solid, white fat at ordinary temperture, having a bland taste and the characteristic cocoanut odor. It is rarely adulterated and is very readily saponified. In recent years the price of this oil has increased materially because cocoanut oil is now being used extensively for edible purposes, especially in the making of oleomargarine and bakers' fats. Present indications are that shortly very little high grade oil will be employed for soap manufacture since the demand for it in oleomargarine manufacture is steadily increasing and since new methods of refining the oil for this purpose are constantly being devised.

The oil is found in the market under three different grades: (1) Cochin cocoanut oil, the choicest oil coming from Cochin (Malabar).

This product, being more carefully cultivated and refined than the other grades, is whiter, cleaner and contains a smaller percentage of free acid than the other grades. (2) Ceylon cocoanut oil, coming chiefly from Ceylon, is usually of a yellowish tint and more acrid in odor than Cochin oil. (3) Continental cocoanut oil (copra). This product is generally superior to the Ceylon oil and may be used as a very satisfactory substitute for Cochin oil, in soap making for example, provided it is low in free acid and of good color.

Cocoanut oil has a saponification value of 246–260, an iodine value of 8–9.5 and the melting point is approximately 22° C. By pressing, cocoanut oil olein and stearin are prepared and the refined stearins are largely used as cocoa-butter substitutes in the manufacture of chocolate and biscuits, also for pharmaceutical purposes. The refined olein finds use as a baking fat in biscuits and pastry. The whole oil is customarily used in making margarine. "Nut oil" and "nut butter" usually have cocoanut oil as their basis.

Japan Wax. See under waxes.

Shea Butter (Shea nut oil). This is a stiff, plastic fat somewhat granular and occasionally of a "stringy" nature. It contains from 5 to 10 per cent of unsaponifiable matter. The refined fat, which can be rendered practically tasteless and odorless, finds an increasing use abroad for edible products.

Animal Fats. Under this head are included those solid fats which are derived from animal tissues. They vary in degree of hardness according to the amount of the glycerides of unsaturated fatty acids present, those with the higher amount being the softer.

Although only non-drying fats will be considered it may be well to state that certain animal fats have quite pronounced drying qualities.

CONSTANTS FOR ANIMAL FATS

Name of Fat.	Specific Gravity.		Saponification Value.	Iodine Value.	Refractive Index.	
Horse	0.9189	15° C	200.5	81–2		
Lard	0.934–0.938	15° C	193.5	66–7		
Beef tallow	0.943–0.952	15° C	190.9	46–55		
Mutton tallow	0.937	15° C	193.2–200	38–46	1.4510	60° C
Butter	0.926–0.946	15° C	192–195.2	35–46	1.4510	60° C

Tallow is the name given to the fat extracted from the solid fat or "suet" of cattle, sheep or horses. The quality varies, depending upon the season, the food and age of the animal and the method of rendering. It comes to the market under the classification of edible and inedible, and is more specifically identified as beef tallow, mutton tallow or horse tallow. The better quality is nearly white and grows whiter

upon exposure to air and light, though it usually has a slightly yellowish tint. It has a well defined grain and clean odor. It consists chiefly of stearin, palmitin with some olein. Tallow is by far the most extensively used and important fat in the making of soap, but by means of the hydrogenation process, tallow-like products are now being made from vegetable oils as well as fish and whale oils which are beginning to replace tallow in soap making.

Beef Tallow. The fat from different parts of the animal are, as a rule, not kept separate during the rendering, except when the tallow is to be used in making oleomargarine. In this case selected fat is rendered at as low a temperature as possible. The oleo stock which is obtained is usually clarified, as by washing with weak brine. The oil is allowed to grain and is then pressed. The fat which is expressed sets to a soft buttery consistency and is known as oleo or oleo oil. The residue is in the form of hard cakes and is termed oleo stearin or beef stearin. In cold weather, when a more liquid oleo oil is required, the pressing is not as thorough, so that both products are softer and the yield of stearin is greater. All the other fatty portions of the animal are rendered to produce the maximum yield of fat. These form the various grades of tallow, most of which goes to the soap maker, but some of the better grades are employed for edible purposes. When fresh, beef tallow is nearly white, odorless and almost tasteless, but the lower grades have a strong odor and flavor. A considerable quantity of tallow finds application in preparing lubricating greases, and leather dressings.

Mutton Tallow. As a rule mutton tallow is harder than beef tallow, although in other respects it is very similar to it. The methods of rendering are about the same as for beef tallow. Mutton tallow tends to turn rancid on keeping, and hence is not often employed in butter substitute manufacture nor preferred in high grade toilet soaps.

Horse Fats. When in a fresh condition horse fat is of a yellowish color, of a buttery consistency, and neutral in reaction. On being allowed to stand for some time it separates into solid and liquid portions. It is now a commercial article owing to the large consumption of horse meat. In some localities it is used for edible purposes in place of lard; its chief use, however, is in the manufacture of soap.

The bleaching of tallow is often practiced and fuller's earth is useful for this purpose. The following procedure shows the method employed. A quantity of tallow is melted and charged into the bleaching tank. The latter is steam jacketed and is provided with a mechanical agitator or a coil for stirring by compressed air. The tallow is heated to 82° C. and 10 pounds of dry salt per ton of fat is added and thoroughly mixed by agitation. The salt coagulates any albumen and dehydrates the fat. The whole mass is allowed to settle for several hours. Any brine which has separated is drawn off from the bottom and the temperature of the fat then raised to 71° C. Fuller's earth to the extent of 5 per cent

of the weight of the tallow is added and the whole mass agitated about thirty minutes.

The bleached fat, containing the earth is pumped directly to a previously heated filter press and the issuing clear oil may be run directly to the soap kettle.

One of the difficulties experienced in the operation is the heating of the press to a temperature sufficient to prevent solidification of the fat without raising the filter press to too great a temperature. To overcome this the first plate is heated by wet steam. Air delivered from a blower and heated by passage through a series of coils raised to a high temperature is then substituted for the steam. The moisture produced by the condensation of the steam is reconverted to vapor by the hot air and is carried on gradually to each succeeding plate where it condenses and again vaporizes. In this way a small quantity of water is carried through the entire press, raising its temperature to 80°–100° C. This temperature is subsequently maintained by the passage of hot air. By this method of heating, the poor conductivity of hot air is overcome through the intermediary action of water vapor and the latent heat of steam is utilized to obtain the initial rise in temperature. The cake in the press is heated for some time after the filtration is complete to assist drainage. After such treatment the press cake should contain approximately 15 per cent of fat.

Lard. By rendering the fat which surrounds the kidneys and bowels of the pig a product is obtained known as "leaf lard." This, however, constitutes only a small portion of the product sold under this name. The following grades are recognized in the trade: *Neutral lard No. 1* which is prepared by rendering the leaf in a fresh condition at a temperature of 50° C. This is used in the manufacture of "oleomargarine"; *neutral lard No. 2* which is obtained by rendering the back fat in the same way as No. 1. It is used by confectioners and biscuit makers. *Leaf lard* is obtained by subjecting the residue from neutral lard to steam heat under pressure. *Choice kettle-rendered lard* is prepared from the residue of neutral lard No. 1 by heating it, together with fat from the back, in steam-jacketed open kettles. *Prime steam lard* is the product obtained from other parts of the hog by rendering in tanks by direct application of steam.

Lard is of a pure white color and has, at ordinary temperature, a salve-like consistence. It is often admixed with beef fat, beef stearin, cotton seed oil, cotton seed stearin, and other vegetable fats and the composition employed as a substitute for pure lard.

Lard "Compound" is made in enormous quantities by thickening edible cotton seed oil with oleo stearine so as to obtain a product of lard-like consistency. Stearin from other sources similarly may be used as a thickener or stiffener and hydrogenated cottonseed oil or "vegetable stearin" is now being used for this purpose.

Butter Fat. This product is obtained from the fat contained in cow's milk, and is used entirely for edible purposes.

Butter Substitutes. The butter substitutes on the market consist of mixtures of animal fats and vegetable fats and oils. They are sometimes colored yellow with annatto or oil soluble yellow. More often no coloring agent is used, as the tax on the colored is much greater than on the uncolored. The animal fats are oleomargarine "oleo oil," or neutral lard. The vegetable oils used are, generally, cotton seed oil and cotton seed stearine. Hydrogenated oils are beginning to be used. In the manufacture of oleomagarine the freshest materials are employed, great cleanliness being necessary. Methods of preparing the oil basis as well as the procedure of working this into oleomargarine vary considerably, but the following will illustrate the character of the operation. Kidney fat is removed from the slaughtered animal as quickly as possible, carefully selected, washed with warm water, and thoroughly cleaned. This selected fat is then rapidly cooled, cut, shredded and ground in a roller mill. The fat thus disintegrated is placed in tin-lined steam-jacketed kettles and heated to 45° C., at which temperature a portion of the fat separates. The mass is clarified by sprinkling in salt and the liquid portion is run off into shallow tin-lined pans; on cooling the bulk of the stearine crystallizes. The cooled mass is then subjected to hydraulic pressure and oleo oil is collected.

The oleo oil, is churned with the vegetable oils and fats, and with "pasteurized" skim milk. The object of churning is to overcome the tendency of the oleomargarine to crystallize. From the churn the margarine is run into cooling tanks where it comes in contact with ice water. The solid mass thus obtained is worked in a kneading machine to remove the water, and it is here colored, and salted to taste. Some manufacturers also add "butter flavor" which consists, for example, of a mixture of propionic acid, butyric acid and caproic acid or ethers. This also makes the margarine upon analysis appear more like pure butter.

Edible oils and edible fats are defined by the Department of Agriculture as such glycerides of the fatty acids as are recognized to be wholesome foods. They are dry and sweet in flavor and odor.

Liquid Waxes

Sperm Oil. The most important member of this class is sperm oil, which is obtained from the head and blubber of the sperm whale. The head oil, which is the more valuable, when first separated is clear and limpid, but changes to a hard mass on standing. The body oil when fresh is of a light straw color. The two oils sometimes are mixed together and allowed to stand for two weeks before refining. The solid portion which separates is removed from the oil by subjecting to hydraulic pressure at 32° F. whereby a clear oil is obtained known as "winter sperm oil."

The press cake is then warmed to about 50° F., and again pressed, thus giving "spring sperm oil." The residue from the second pressing is allowed to stand for several days at a temperatrue of about 80° F. It is then subjected to hydraulic pressure, whereby "taut-sperm oil" is the result. The oils obtained from these three pressings vary in color from pale yellow for the refined oil to brown in the last named product. No. 1 sperm oil is a high grade of body oil and is very pale, almost water white in color. No. 2 sperm oil is darker and usually has an orange color.

The specific gravity of sperm oil at 15° C. varies from 0.8799 to 0.8835; (0.8820 being a fair average value) its saponification value from 125.2 to 132.6; and its iodine value from 81 to 90. It is used as a lubricating oil and in leather finishes. The extent of the latter use depends upon the price of lard oil. Sperm oil contains practically no glycerine.

The term "spermaceti" is sometimes commercially used to refer either to the head oil containing spermaceti, or to the head oil with its content of spermaceti mixed with a certain amount of body oil.

Solid Waxes

Carnauba Wax. This is a very hard, sulphur-yellow, or yellowish-green substance, melting at about 84°, of nearly the same specific gravity as water, and leaving, on ignition, a trifling quantity of ash, which often contains iron oxide. It is a wax which exudes from the leaves of the Corypha cerifera, a palm tree growing in Brazil and a few other South American countries. The white powdery mass which is scraped off from the sun-dried leaves is thrown into boiling water, thus melting the wax which collects as a solid mass on cooling. The crude product is dark in color, but on refining becomes much lighter. It has a specific gravity of from 0.990 to 0.999; the saponification value being from 79 to 95; and the iodine number about 13.5. When heated the wax gives off an agreeable aromatic odor. The principal use of carnauba wax is in floor waxes, polishing pastes and for raising the melting point of soft waxes. It is sometimes used in phonograph cylinders and for candlemaking.

Candelilla Wax. This wax is found coating the surface of a plant which grows in great abundance in the northwest of Mexico and Southern Texas. The common name given to this plant by the Mexicans is candelilla. According to competent botanical authorities it is in all probability euphorbia antisyphilitica. The plant (which is reported to be abundant over large areas of this section where it grows as bunches of leafless, reed-like stems 2 to 4 feet high and from $\frac{1}{4}$ to $\frac{1}{2}$ inch in diameter) is covered with waxy scales which appear to have the function of sealing moisture within the plant structure. The wax is partly in combination with lime, and extraction is effected by boiling with a 2 per cent solution of sulphuric acid. Several factories are operating in Southern Texas and in the Chihuahua region of Mexico. The wax may also be obtained

by immersing the plant in boiling water when the wax separates and rises to the surface. Obtained in this manner it is usually of a dark-brown color due to the presence of minute fragments of bark and other foreign matter. When refined the wax is opaque to translucent and of a brownish yellow color. The wax is harder than beeswax but not as hard and brittle as carnauba wax. The specific gravity of the well-refined wax is .983, melting point 67–68, saponification value 65, iodine number 37, and the refractive index 1.4555 at 71.5° C. Candelilla, like carnauba wax, is used in polishing compositions and for raising the melting-point of softer waxes.

Japan Wax. This is a hard tallow-like mass which surrounds the kernels of the berries of several varieties of sumach trees found in China and the western provinces of Japan. The berries are collected and stored until they have fully matured, then are crushed and winnowed to separate the husks. The powdered mass so obtained is put into sacks and subjected to pressure. The berries yield from 15 to 25 per cent of a greenish, tallow-like mass which is refined by remelting and filtration. The wax is bleached by exposure to sunlight, just as is done in the case of beeswax. Japan wax brought to this country is usually of a pale yellow color and although quite hard has a slightly sticky feel and possesses a characteristic odor. When the wax has been kept for a long period it acquires a rancid smell. It is said that perilla oil is used as an adulterant.

Japan wax consists chiefly of palmitin and free palmitic acid. The free fatty acids vary considerably, but range from 4 to 12 per cent or higher. The specific gravity ranges from 0.975 to 0.984. The saponification value is about 220 and the iodine number from 4 to 15. Being a glyceride Japan wax is readily distinguished from the true waxes by its saponification value and by yielding glycerine on saponification. The wax is sometimes adulterated with a considerable proportion of water ranging as high as 30 per cent. Its principal use is in floor waxes, as a constituent of various polishes and dressings and in finishing leather.

Chinese Wax. This material, also known as insect wax, is a secretion of an insect inhabiting a variety of evergeen tree found in China. The wax is yellowish white in color and is nearly odorless and tasteless. It resembles spermaceti in appearance, but is considerably harder. Insect wax is used for making candles, for polishing purposes and as sizing for paper and cotton goods, but on account of its extensive use in China it does not find its way to our country to a large extent.

Myrtle or Bayberry Wax. The wax is obtained by boiling the berries of various species of Myrica with water. The wax has a green color due to chlorophyll, but may be bleached on exposure to sunlight or air. The fatty acids of this waxy material consist chiefly of palmitic acid. The saponification value is 205 and the iodine number 2–4. The wax is prized for use in the manufacture of so-called bayberry tallow candles. The production of these candles forms a minor industry on Cape Cod, Mass., and elsewhere.

Wool Wax, Lanolin. In the scouring of wool, preparatory to spinning, a product called wool fat or wool wax is obtained. This is usually removed from the fleece with solvents. The crude product finds application in the currying of leather; while the purified product "lanolin" is used in pharmaceutical preparations. The preparation of lanolin is a complicated operation and much secrecy is maintained with regard to the precise methods employed. In addition to wool fat of this character there is also a so-called degras which is recovered from the suds of wool washing machines and contains the fatty acids of the soaps used in scouring the wool. Mixtures of wool fat and degras with stearin and sometimes paraffin wax are found in the market under various trade names and find their chief use in the leather industry. A good grade of lanolin is now made in this country.

Beeswax. This product is secreted by the honey bee, and serves as the material for building up the honeycomb. The comb is melted in hot water, strained to remove impurities, and subjected to hydraulic pressure. The press cake is boiled a second time and again pressed. Beeswax is of a yellow color, and practically tasteless.

Spermaceti. This wax occurs in the head cavity and the blubber of the sperm whale. Its method of preparation is indicated under sperm oil of which it constitutes the largest part of the solid portion. In the refined condition it forms white lustrous masses, is very brittle and can be easily rubbed into a powder. Its chief use is in the manufacture of candles.

Shellac Wax. In bleaching shellac the raw lac is dissolved in aqueous alkali and a hard waxy material separates which is much prized for use in polishing compositions and shoe blackings. The wax resembles carnauba wax in polishing qualities. Shellac wax possesses a brown to yellow color and when heated gives off an odor suggestive of shellac.

Montan Wax. By extraction of the lignites found in Saxony and Thuringia by means of volatile solvents, a waxy material known as montan wax is obtained. The crude wax is of a dark brown color, but by distillation with superheated steam a white or nearly white product melting above 70° C., is obtained. Montan wax is finding a constantly increasing field of application as a substitute for carnauba wax in shoe polishes and other polishing preparations and for raising the melting-point of softer waxes. For some purposes it is preferred to carnauba wax owing to its lighter color.

Non-inflammable Artificial Wax. The substances to which have been given the trade names of Halowax Oil and Halowax, are chlorine substitution products of naphthalene having the properties of non-inflammability, high boiling points, and a wide range of melting points. One of them, Halowax Oil, remains fluid at very low temperatures, and is heavier than water. The others are wax-like substances, some highly crystalline and others nearly amorphous: they have a faint aromatic

odor sometimes suggestive of naphthalene. All of these are insoluble in water and are quite inert to most aqueous acid and alkaline solutions. They are more or less soluble in common organic solvents, such as benzol, carbon tetra chloride, acetylene tetra chloride, gasolene, naphtha, acetone, hot alcohol, etc. They are all good solvents for sulphur and chloride of sulphur when heated therewith. The melting point of the solid forms varies between 60° C. and 135° C. The boiling point varies between 260° C. and 400° C. They are all good electrical insulators. When in the fluid or molten state, they are of very low viscosity and readily impregnate cellular tissues and porous bodies. Wood and fabric when impregnated with these bodies become non-inflammable. The higher chlorinated products are especially efficient in rendering organic bodies non-inflammable. A notable property of some of these chlorination products is their small contraction during solidification, and their low-coefficient of expansion, compared with natural waxes.

For a more detailed account of the properties, preparation and uses of oils, fats and waxes consult "Chemical Technology and Analysis of Oils, Fats and Waxes," J. Lewkowitsch, Fourth Edition, 1909, and Volume I of Fifth Edition. Macmillan & Co.

Bleaching Oils with Fuller's Earth. So extensive has the practice of using fuller's earth as a bleaching agent become that this earth is by far the most important oil bleaching medium employed at the present time.

Fuller's earth is a variety of clay that has high capacity for adsorbing basic colors and can remove these colors from solution in animal, vegetable, or mineral oils, as well as from some other liquids, especially water. It is valuable when its adsorptive powers are strong enough to permit it to compete actively with fuller's earth already accepted as of standard quality for refining oils.

Analyses of various samples of fuller's earth vary so greatly that chemical analyses are now well understood to be no criterion whatever in determining whether or not a particular clay shall be classified as a fuller's earth. Like all other clays, fuller's earth is a hydrous, aluminium silicate containing small proportions of other substances. Most fuller's earths contain a higher percentage of water of composition than most clays, but this water is not an essential factor in the bleaching properties of all fuller's earths; some bleach fully as well after it has been driven off as before, and others lose much of their bleaching power when this water is removed.

Though samples of fuller's earth from different parts of any one deposit, or indeed from any one locality, are much alike, samples from different localities are so different in their physical properties that it is by no means easy to classify them. To determine whether or not a particular clay is a fuller's earth is no simple matter, for its bleaching power is practically the only characteristic by which it may be identified.

The range of specific gravity of fuller's earth is much the same as

that of other clays, although the apparent specific gravity varies widely, owing to variations in porosity. Fuller's earth, as a rule, is lighter and more porous than other clays. However, both the English earth and the Arkansas earth, when dry, are fully as dense as ordinary clay. The volume that a given weight of fuller's earth occupies varies widely, and a cubic foot of dry, ground fuller's earth from Georgia or Florida weighs only a little more than half as much as a similar volume of English or Arkansas earth. This fact should be taken into careful consideration in applying fuller's earth to the bleaching of oils, for if the same measures are used in a comparative test of different fuller's earths no valid conclusions can be reached.

Most samples of fuller's earth give more or less taste and odor to edible oils but they vary greatly in this respect. For many years the English earth was preferred chiefly because it gave little effect, but methods for removing taste and odor are now well known to all oil refiners, so that the question is not so important as formerly.

Why taste and odor should be imparted to oil by fuller's earth is not known, but it certainly is not generally due to any soluble material in the earth, but rather to some oxidizing action upon the oil itself. This property appears to be connected with the "acidity" of the earth, for if fuller's earth is treated with lime water this action is greatly reduced. Unfortunately, the bleaching power is destroyed at the same time. Certain fuller's earths have so marked an oxidizing action on edible oil that they cause the oil to catch fire spontaneously when air is blown through the filter presses to remove the adhering oil, as is done in practice. This property is fatal to the use of a fuller's earth in refining edible oils, for beside fire risks to buildings it invariably destroys the cloths of the filter presses. Fortunately, only earth from one or two deposits has this property highly developed.

The method used in bleaching edible oils is essentially the same in general principle for all oils, but differs in detail. The temperature at which the bleaching takes place and the proportion of earth used vary not only with every oil, but also in the practice of the various refining plants as applied to similar oils. As cottonseed oil is by far the most important of those oils to which the process of refining is applied, it can best serve as an example.

Crude cottonseed oil is not affected by fuller's earth and it must first be subjected to the usual treatment with an alkali, which removes the fatty acids and at the same time converts the coloring matter into basic forms. Fuller's earth has no power to remove color from cottonseed oil until the crude oil has been treated with an alkali.

Partly refined samples of different cottonseed oils require very different quantities of the same fuller's earth to remove the color. Accordingly, in the best practice, the oils that will require the least quantity of fuller's earth are selected by laboratory tests for bleaching.

With the finest qualities of cottonseed oil as little as $1\frac{1}{2}$ per cent of the best fuller's earth may give an effective bleach; with others as high as 6 per cent is required. Probably 3 per cent of fuller's earth is a fair average for bleaching cottonseed oil at the present time. The proportion of earth used also depends upon the temperature to which the oil is heated before treatment, although too great an increase in temperature may have a deleterious effect on the oil. In fact, it has been the practice of one plant to use in bleaching oils of special quality as much as 10 per cent of fuller's earth and a very low temperature.

In ordinary practice a measured quantity of the dry cottonseed oil is placed in a large vat containing steam pipes and heated to near the boiling point of water. The oil is then rapidly stirred by paddles and the necessary measured quantity of fuller's earth is added. Within one or two minutes the fuller's earth has been thoroughly mixed with the oil by the rapid agitation. The mixture is then run immediately to the filter presses and the fuller's earth filtered out. The quantity of oil for a single operation is so gaged that when all of the oil taken has passed through the filter press, the press itself is charged with fuller's earth and is ready to be opened. Before the press is opened, as much oil as possible is blown out with steam and the oil is generally further removed by blowing air also through the press.

The color of the oil after treatment with fuller's earth is greatly reduced and its standard is determined by means of the tintometer. Treatment with fuller's earth, however, besides reducing the color, also gives more or less taste and odor to the oil, which must be removed before the oil can be marketed.

This taste and odor is developed in oil by any fuller's earth so far found, but the extent of the action varies greatly with fuller's earth from different localities. English earth was long in special favor for refining edible oil because it imparts comparatively little taste and odor, but there are domestic earths that are equal to English earth in this respect, and just as good as regards bleaching qualities. However, the earths that bleach oil the best almost invariably give the greatest taste and odor to the oil, but this is not now nearly so serious an objection as formerly, as methods for removing taste and odor from edible oils are well known.

In the treatment of lard and lard oil it is seldom if ever necessary to use more than one per cent of fuller's earth and generally the lard is not deodorized afterwards.

In determining the decolorizing power of fuller's earth for use for edible oils a quantity of oil should first be selected which is sufficient for all of the tests to be made, as different samples of oils are bleached very differently by the same earth. With cottonseed oil a definite quantity of oil is weighed or measured, placed in a beaker, and heated

(preferably in a water bath) to 100° C. The sample of fuller's earth unless already ground, is first carefully pulverized, preferably in a coffee mill, to pass a 100-mesh sieve. A portion of the pulverized sample, ordinarily 5 per cent of the quantity of oil taken, is weighed and stirred into the hot oil. The stirring is continued for three minutes. The mixture is immediately filtered into a sample bottle, such as is universally used in testing for oil color. If at the same time it is desired to determine the quality of the earth as regards its action in the filter presses, its filtration should take place on a Buchner funnel, using suction. If the question of filtration is not of moment, it is usually simpler to filter through an ordinary steam-jacketed funnel, using filter paper. A portion of the same sample of oil is then treated with a sample of standard fuller's earth, for which purpose the English earth is universally used, and the colors of the two oils obtained are compared in a colorimeter by means of Lovibond color glasses. The only glasses required are the red and yellow series. (Parsons.)

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CHAPTER XXV

LINSEED OIL

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Linseed oil is obtained from the seed of the flax plant. Technically, domestic seed is usually known as *flaxseed*, and the imported seed as *linseed*. The flax plant is remarkable, in that it is grown for either its fibre or its oil; but, apparently, it can not be grown for both at the same time. If grown for seed, the fiber is of small value; and if grown for fiber, the seed is immature. It is also remarkable for the range of climate in which it can grow. It is grown in North Dakota, Northern Russia, The Argentine, Southern Russia, and India. The flax plant has the reputation of poisoning the soil where it has been grown for any length of time. Professor Bolley of the North Dakota Agricultural Station has stated that this poisoning is due to bacteria and that it can be avoided, largely, by using seed on which the bacteria have been killed by formaldehyde, by avoiding contaminated seed, and by using seed which has been rendered immune by a selective process of growth.

The World's Production. The World's Production of the Seed of the Flax Plant for the Year 1913, by the Chief Producing Countries.

U. S. A.	Bushels.
North Dakota	7,200,000
Montana	3,600,000
Minnesota	3,150,000
South Dakota	3,060,000
Kansas	300,000
Iowa	263,000
Wisconsin	126,000
Nebraska	54,000
Missouri	50,000
Colorado	50,000
U. S. A. (total)	17,853,000
Canada	17,539,000
Argentina	39,600,000
India	21,428,000
Russia (estimated)	22,000,000
Total	118,420,000

The bushel of flaxseed weighs conventionally 56 pounds. The quantity of oil in clean, hand-picked seed varies with the locality of its production and the size and maturity of the individual seeds. The following figures give the approximate range of oil contents, as determined by careful extraction, in clean, hand-picked seed from various sources:

North American seed-oil	36.50–40.00%
Calcutta and Bombay seed-oil	37.50–42.00%
Argentine seed-oil	36.00–39.00%

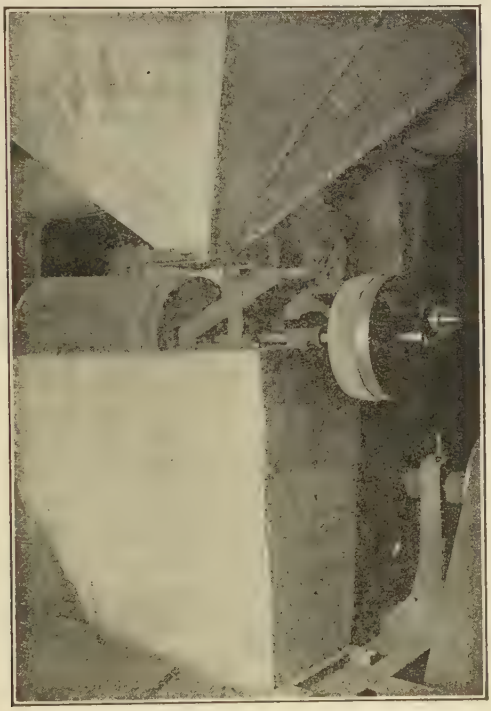

Fig. 290.—Flaxseed Sifter.

Methods of Production. Linseed oil is produced to-day in three different ways:

1. By the *Old Method* of grinding, heating, and pressing by hydraulic pressure—the residue being left in the form of cake, known as *linseed oil cake*. The temperature of the meal, as it leaves the heaters, varies considerably in practice. The meal can be run cold, and cold-pressed linseed oil produced, or the heat can be as high as 180° F. In ordinary practice, the heat is something over 160° F. The oil left in the cake runs from 5.5 to 6.5 per cent.

2. By the *Anderson Expeller Mill*, in which the meal is heated only slightly and is forced by a screw through a conical grating—the oil com-

ing through the grating, and the meal, formed into scales like cocoanut shells, coming out at the end of the expeller. The oil left in the scales or shells sometimes exceeds 8 per cent.

3. By the *Extraction Process*, wherein the ground seed is leached with light petroleum naphtha, which dissolves the oil, leaving a meal containing usually less than 4 per cent of oil. The naphtha extract is distilled, the naphtha recovered and used over again, and the linseed oil obtained as a residue from this distillation.

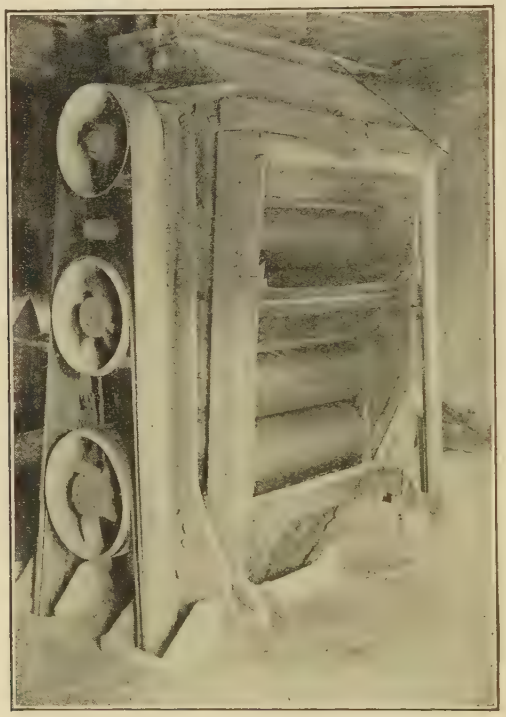

Fig. 291.—Flaxseed Crushing Rolls.

All three processes give commercially pure raw linseed oil. The relative values of these products are not far apart.

Characteristics of Linseed Oil. Linseed oil is a saponifiable oil—that is to say, it contains radicals of fatty acids and glycerine in combination. Under the influence of alkali it is decomposed—glycerine is liberated and soap is formed. The fatty acids of linseed oil give it its character. Some of these acids are what is known as "unsaturated," that is, some of the chemical bonds are unsatisfied. This gives linseed oil its power to absorb oxygen from the air, the oil increasing in specific gravity and, ultimately, if exposed in thin films, becoming changed into a hard, horny mass. In this "drying" operation, the change is not, however,

one of simple oxidation, although that is probably what takes place initially. During the oxidation, carbonic acid and water are given off, together with other gases and volatile substances.

In the drying of linseed oil it has been generally recognized that it increases in weight and also in specific gravity. Sabin has shown, however, that the increase in weight only takes place up to a certain point, after which there is a loss in weight, so that at the end of 180 days, in his experiment, the linseed oil had come back to its original weight. Inasmuch as the oil had increased in gravity, there was an actual loss in volume during the oxidation changes which took place.

It is convenient to consider the product of the drying of linseed oil under the single name "*linoxyn.*" This product is, however, composed of many constituents and it would appear that the oxidation process is continuous and perhaps never complete. Dried linseed oil—linoxyn—is tough and elastic and is the principal constituent, in volume, of almost all dried paint films.

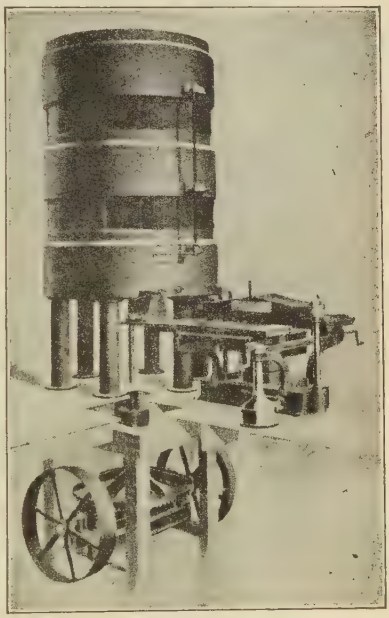

FIG. 292.—Heater and Cake Former.

The chemical constituents of raw linseed oil are only approximately known. It is believed to be composed of the glycerides of the following fatty acids:

Palmitic Acid, $C_{16}H_{32}O_2$. About 5.0 per cent of its glyceride is present. Palmitic acid is a saturated acid of the acetic series.

Myristic Acid, $C_{14}H_{28}O_2$. About 5.0 per cent of its glyceride is present. Myristic acid is a saturated acid of the acetic series.

Oleic Acid, $C_{18}H_{34}O_2$. A small amount of this acid is probably present. It is the characteristic acid of the $C_nH_{2n-2}O_2$ series.

Linolic Acid, $C_{18}H_{32}O_2$. It is the characteristic acid of the $C_nH_{2n-4}O_2$ series.

Linolenic and Isolinolenic Acids, both of the formula $C_{18}H_{30}O_2$. They are characteristic of the $C_nH_{2n-6}O_2$ series.

The percentages of the glycerides of linolic, linolenic, and isolinolenic acids present in linseed oil differ in the opinion of various investigators. (See Lewkowitsch, Vol. II, pp. 50–52, 1909 Ed.)

Raw and unrefined linseed oil, as usually produced, contains a small amount of mineral matter consisting of phosphates of calcium and

magnesium in combination with nonoleaginous organic matter probably carbohydrates (mucilage), which are present so abundantly in flaxseed. When such an oil is heated to something over 350° F., it is said to "*break.*" The oil thickens and becomes filled with a cloud. If this cloud is filtered out and washed with petroleum ether, it is found to be composed, to a large extent, of the phosphates referred to above—the oil itself is freed of these phosphates. The amount of ash in raw and unrefined linseed oil runs from 0.08 to 0.25 per cent.

FIG. 293.—Hydraulic Press.

A measured gallon of linseed oil weighs 7.78 pounds. Custom, however, has established the practice of selling linseed oil on what is called the "weighed gallon" of 7.5 pounds. This, however, relates only to oil sold in lots based on barrel deliveries, and not to the small quantities sold in the retail trade.

Linseed Oil in Paints. The use of linseed oil in paints has for its purpose the binding together of the particles of pigment into a more or less solid mass when the paint is dried by exposure to the oxidizing influence of the atmosphere. The degree of gloss which a dried paint possesses is mostly dependent upon the relative amount of oil present,—thus, in gloss paints, considering only the oil and the pigment, the percentage

of oil by volume is usually something over 66 per cent, the pigment being something under 34 per cent, whereas in paints having a low gloss, known as " flat paints," considering only the oil and the pigment, the percentage of oil by volume may be less than 50 per cent, and the pigment over 50 per cent. In some flat paints there is less binding material than this, but good results with respect to wear are not obtained in this way.

Linseed oil, as produced by the old process and the Anderson Expeller, is somewhat cloudy as it comes through the press, due to suspended particles of linseed meal. The oil is usually run through cloth-covered filter presses, which remove the suspended matter. A certain amount of mucilage, however, remains dissolved in the oil, which may settle out, on tanking, in the form of " foots," so that the best practice is to allow linseed oil to cool in tanks, after which it is filtered through paper before

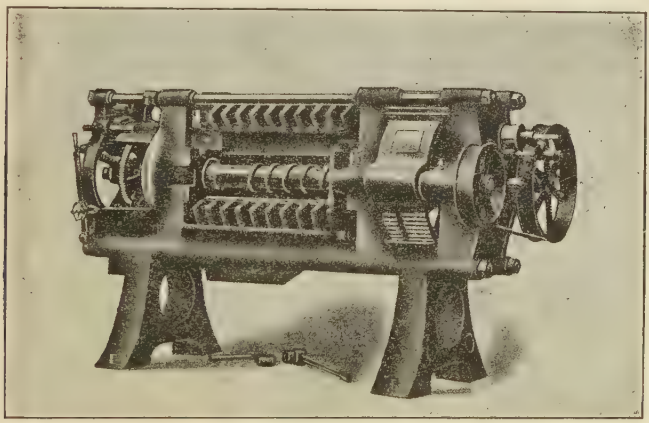

Fig. 294.—Filter Press.

shipment. Even then, linseed oil will, on standing, tend to show a small separation of foots, which may accumulate in the bottom of barrels or tanks. For most industrial purposes the oil should be as clear and free from foots as practicable. In certain kinds of paints, however, such as roof paints, the linseed oil foots are less objectionable, and it is customary to use foots in the preparation of such paints.

Color of Oil. The color of raw linseed oil varies somewhat according to its origin. Oil from East Indian seed is comparatively light in color, while oil from seeds grown in colder climates is about the color of amber. This color is due to certain resinous substances present, principally in the shells of the seed, which, in the process of crushing become dissolved in the oil. Under the influence of light, linseed oil bleaches out, the brown tone disappearing, and the yellow also becoming reduced in intensity. For this reason, the color of the oil used in paints to be exposed to the sunlight, as in the case of exterior paints, is of small importance. Even

in white paints, the oil bleaches out under the influence of the sun-light and does not affect unfavorably the color of the paint. In paint used on interiors, this is not the case, however, and it is usual to select oils light in color, which lightness of color is obtained by proper bleaching and refining.

Paints containing linseed oil, and in fact most vegetable oils, tend to turn yellow in dark or poorly lighted places. The tendency to yellow is somewhat affected by the pigment and also the amount of oil present. The cause of this tendency of interior paints to turn yellow has been variously explained. Mulder intimated that it was due to the absorption of moisture in forming a hydrate of the linoxyn. This may or may not be true, and from investigations carried on by the writer, it would appear mostly due to the action of the ammonia in the atmosphere. This does not, however, explain the mechanism of the yellowing.

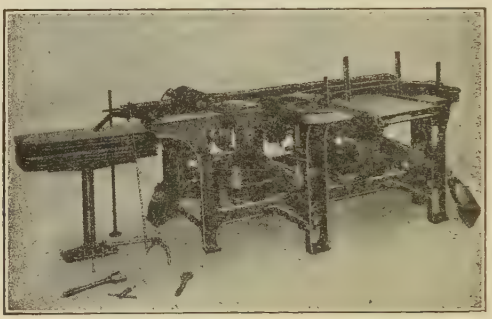

Fig. 295.—French Linseed Cake Trimmer.

Refining of Linseed Oil. The refining of linseed oil is usually accomplished by treatment with sulphuric acid somewhat after the following manner: The oil, amounting to about 500 gallons, is placed in a tank provided with either mechanical or air agitation. Strong sulphuric acid, 60–66° Bé., equal to about 1 per cent by weight of the oil to be refined, is allowed to flow slowly into the oil. The agitation is kept up for some time; the oil turns to a muddy green. It is then allowed to settle, the sulphuric acid sludge coming together in large flocks and separating out. After standing over night, the clear oil is drawn off, some water added, and the whole mass agitated with live steam. The oil tends to form something of an emulsion in the beginning and, after a while, becomes clear. It is then allowed to settle, the acid water drawn off, and another steaming given, if thought necessary. The oil is then drawn into storage tanks, and the remaining water allowed to settle out; the clear oil is drawn off for use. In this operation the mucilaginous matter and some of the coloring matter, referred to above, are removed. The oil has also increased in acid number, that is to say, its contents of free fatty acids has increased. Refined oil is similar in properties to raw linseed oil,

except that it is less viscous. It is free from the phosphates referred to above and usually contains over 4 per cent of free fatty acids, figured as oleic acid. The bleaching of linseed oil is also accomplished by exposure to the sunlight in shallow pans, and also by the use of fuller's earth. The usual process, however, involves the sulphuric acid treatment referred to above.

Drying Properties. Linseed oil belongs to the general class of oils known as " drying oils." This property of *drying*, already referred to, consists in the oxidation of the oil and the formation of more or less solid, hard products. Linseed oil has this property more conspicuously than any of the other so-called " drying oils." It has been found, however, that in the case of raw linseed oil, which will take from four to five days to dry hard in a thin film, this drying rate can be increased by

Fig. 296.—Oil Cake and Meal.

the addition of certain metallic oxides, such as lead oxide and manganese oxide. By the proper addition of these oxides, linseed oil can be made to dry to the touch in from four to eight hours. It appears that lead and manganese in a great variety of forms can be added to linseed oil and give to it its increased rapidity of drying. However, to give the best results, they should become completely dissolved in the linseed oil. For pratical purposes, excellent drying results are obtained when the linseed oil contains oxide of lead (PbO), .20 per cent and oxide of manganese (MnO), .05 per cent.

Boiled Linseed Oil. Boiled linseed oil is an oil to which a sufficient quantity of lead and manganese oxides has been added, and, by the action of heat, these oxides have been made to dissolve in the oil. The old practice was to boil the oil in kettles over an open fire, and this practice still obtains to some extent, although probably the temperature to which the oil is now heated seldom reaches that to which boiled oil in the old days was subjected. The term " boiled " as applied to linseed oil is not,

strictly speaking, correct. Linseed oil does not boil in the same sense that water does, but, when heated to a sufficiently high temperature, suffers destructive distillation, some of the glycerine being driven off in the reduced form known as "acrolein." There are also other decomposition products produced. In modern practice, the manufacture of boiled oil starts with the production of a concentrated boiled oil containing a comparatively large percentage of lead and manganese oxides, such concentrated boiled oil being known as a "crushers drier." The concentration is such that when one part of this crushers drier is added to 16 parts of raw linseed oil and the mixture heated to bring about complete incorporation, boiled linseed oil of commerce is obtained. The temperature of heating considered by the writer most desirable is about 350° F. Not all boiled oil is, however, heated to this temperature. In some cases the temperature reached is only that which can be obtained by a steam coil. In some cases, the driers used are resinates of lead and manganese, which, if the amount of rosin present is not too great, produces good merchantable boiled oils. The temptation, however, to overload the resinate driers with an excess of rosin has made this practice questionable in the minds of some. In the preparation of boiled oil, red lead has some advantage over litharge in that the lead oxide stays in solution better where red lead is used. The black oxide of manganese, the dioxide, used should be in a very fine state of subdivision, so that it will dissolve completely in the oil on the application of heat. For the production of particularly light-colored boiled oils, borate of manganese and acetate of lead can be used, or linseed oil soaps of lead and manganese can be produced in the wet way, and these dissolved in the oil by the application of heat.

Linseed Oil Constants. It is customary to speak of the various figures obtained from the testing of linseed oil as its "constants." This word is unfortunate, inasmuch as the figures are anything but *constant*. Linseed oils of various origin differ very much in the so-called "constants" obtained, and the same linseed oil may have its constants changed by slight oxidation. The best and most authoritative figures on linseed oil, and the methods of testing, have been published in the reports of Committee D-1 of the American Society for Testing Materials, whose specifications for oil from North American seed have been carefully worked out. They are as follows:

	Maximum.	Minimum.
Specific gravity at $\frac{15.5° \text{ C.}}{15.5° \text{ C.}}$	0.936	0.932
or		
Specific gravity at $\frac{25° \text{ C.}}{25° \text{ C.}}$	0.931	0.927
Acid number	6.00	
Saponification number	195	189
Unsaponifiable matter	1.50	
Refractive Index at 25° C.	1.4805	1.4790
Iodine number (Hanus)		178

Oil from Baltic seed apparently has a slightly higher iodine number than that from North American seed. Oil from East Indian seed is slightly lower in iodine number, and oil from South American, or La Plata, seed is considerably lower in iodine number. It may be difficult, therefore, at times to judge simply from the analytical results obtained whether a linseed oil is strictly pure, if its origin is not known. Some recent work done by Eibner (Farben-Zeitung Oct. 12, 1912 *et seq.*) indicates that the hexabromide test is of great value in determining the value of linseed oil.

Driers. In order to accelerate the speed of drying of raw linseed oil, it is a common practice for the painter to use "driers." These are preparations usually liquid but sometimes in paste form, consisting of lead and manganese soaps dissolved in turpentine or benzene, in the case of liquid driers, and mixed with pigments and oil, in the case of paste driers. Liquid driers, while very variable in composition, usually contain lead and manganese compounds in such quantity that one (1) part of the drier added to sixteen (16) parts of raw linseed oil will make the oil dry to the touch in from 8–12 hours. Boiled linseed oil should require the addition of no liquid drier. Raw linseed oil, to which liquid drier has been added, is sometimes sold as boiled oil. Such a mixture, as it has not been subjected to the proper heat treatment, is not a true boiled oil. Derisively, it is known as "Bung Hole Boiled Oil." Its sale as boiled oil is clearly deception.

Adulteration. Linseed oil is occasionally adulterated with mineral oil and rosin oil, and when the price permits it, with non-drying oils such as Soya Bean Oil, etc. The presence of mineral or rosin oil in linseed oil is easily detected, as they remain in the unsaponifiable matter determined in the usual course of analysis. The presence of non-drying or semi-drying oils is more difficult of detection. Their presence is indicated by a low iodine number and a low specific gravity.

Application. Outside of use in paints, linseed oil has its principal use in the preparation of varnishes, lithographic oils, and linoleum. In varnishes, the oil used is usually prepared so that it will not "break." It is then "bodied," that is, increased in gravity and viscosity to the degree particularly desired by heating in kettles to about 550° F., whereby some of the glycerine is driven off, and the oil, to a greater or less extent, polymerized. Such an oil mixed with melted gums and driers and thinned with turpentine or benzene, produces the oleoresinous varnishes of commerce, which vary according to the kind of gums used, the degree to which the oil has been bodied, and the proportioning of the various constituents.

Linseed oil simply bodied by heat is used for the preparation of lithographic inks. The bodying of linseed oil can also be accomplished by blowing. The oil is heated to above 250° F., and a current of air is passed through it. Blown oils dry harder than oils bodied simply by heat.

Oil Cake. Oil cake and linseed meal are by-products of the manufacture of linseed oil. They are valuable cattle foods and contain:

Oil or "Crude Fats"	4– 8%
Albuminoids or "Crude Protein"	31–40%
Crude fibre	8–12%

The remainder consists of carbohydrates and mineral matter. As a cattle food, it is too rich and has to be mixed with other food materials containing more crude fibre, etc. Comparatively little oil cake and meal are consumed in this country, most of it being shipped to Europe.

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CHAPTER XXVI

THE HYDROGENATION OF OILS

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In the presence of a suitable catalyzer oleic acid and hydrogen combine, molecule for molecule, to yield stearic acid according to the equation, $C_{18}H_{34}O_2+H_2=C_{18}H_{36}O_2$. Thus 282 pounds of oleic acid require 2 pounds (or about 0.7 per cent.) of hydrogen for the production of 284 pounds of stearic acid, and similarly the transformation of olein into stearin requires the use of about 0.68 per cent of hydrogen. One thousand cubic feet of hydrogen weigh approximately 5.6 pounds, hence a pound of olein calls for a little over 0.1 of an ounce of hydrogen equivalent to approximately 2500 cubic feet of hydrogen per ton of olein (of 2000 lb.). Thus by weight only a relatively small quantity of hydrogen is needed.

Catalyzers. Those bodies which modify reaction velocity without stoichiometrical participation in the reaction—find another important industrial application in the hydrogenation or "hardening" of oils.

Catalyzers recognized as useful for the purpose are nickel and palladium, although platinum, copper, iron, and other metals have been used to some extent. Nickel oxide also has been employed. As nickel is probably the most important of these catalyzers, in view of its efficiency and relatively low cost, it will be first considered.

The preparation of an effective nickel catalyzer requires considerable care. The oxide or hydroxide of nickel is first obtained by ignition of nickel nitrate or precipitation of nickel hydroxide from a nickel solution by the addition of an alkali. Obtained in this way or in any other suitable manner, the next step is the reduction to metallic nickel. For this purpose the nickel is placed in a receptacle which may be heated controllably and hydrogen gas is passed over the mass at a temperature ranging from 250 to 500° C., or so, until water is no longer evolved.

The most sensitive catalyzers are obtained by reduction at the lowest possible temperatures. Nickel begins to reduce below 220° C., but at 270° C. the reduction is not complete even after long duration of exposure to hydrogen. A temperature of 300 to 325° C. gives fairly complete reduction and is a satisfactory working temperature. The lower the temperature at which the nickel is reduced, the more sensitive it is to

various external influences, hence the preparation of this catalyzer should be conducted not only with respect to degree of activity, but also with respect to longevity. Nickel is easily poisoned by chlorine and by sulphur in the sulphide form. Copper is much less sensitive to poisons than nickel, but, on the other hand, it is much less active.

Catalyzer made from the oxide without supporting material, weight for weight, is hardly as efficient as when the active surface is increased by the use of a carrier. Hence we find many proposals for the production of catalyzers with a great diversity of carriers, ranging from pumice stone and kieselguhr to charcoal and sawdust.

After nickel has been reduced as described above, it should be kept out of contact with air, as it is extremely pyrophoric and loses in efficiency on exposure to the air. Consequently, when treating oil with such a catalyzer, it is advisable to free the treating apparatus from air by flushing with hydrogen.

Several forms of treating apparatus are in use, all of which have the same object in view, viz., to secure intimate contact of hydrogen gas with the oil and catalyzer. This is accomplished in various specific ways, one method being to spray the oil mixed with catalyzer into a chamber containing hydrogen and to continue the spraying operation until the requisite degree of hardness is reached. By another method the oil and catalyzer are violently agitated in a closed receptacle in the presence of hydrogen. Still another system provides for the simple operation of bubbling the hydrogen gas through a body of oil and catalyzer, any unabsorbed gas being collected and reused.

A great variety of fatty oils may be hydrogenated to yield useful products, but the process is finding application especially in the hardening of vegetable oils such as cottonseed, corn, sesame, castor and linseed oils and marine animals oils such as fish and whale oils. The analytical constants of oils of course change as hydrogenation proceeds and aside from the increase in melting point, the progress of the reaction is indicated by a gradual reduction in the iodine number and index of refraction, while the specific gravity increases as a rule.

Hydrogen. One of the problems in the hydrogenation field is that of a cheap supply of pure hydrogen. The demand for hydrogen in various directions has increased of late and has led to improvement in the manufacture of the gas.

The two methods now most favored in the hydrogenation of oils are the iron sponge steam process and the electrolytic method. For vary large plants the iron sponge steam process is preferred, but it is relatively complicated and scarcely to be recommended for plants calling for 1000 cubic feet of hydrogen, or less, per hour. Hydrogen also is obtained from water gas by liquefaction of the carbon monoxide according to the Linde system and separation of the hydrogen from the liquefied monoxide.

Uses of Hydrogenated Oils. The ability to prepare from ordinary liquid fatty oils a fatty body of almost any desired degree of consistency, renders hydrogenation especially attractive in the production of edible fats and soap making materials. These are, undoubtedly, two of the most important applications, although hydrogenated oils are likely to have a rather wide use in the arts. In the manufacture of lubricants and tanner's greases, for example, the hydrogenated fats may be used to advantage.

Uses of Hydrogenated Oils in the Soap Industry. By hydrogenation, oils which formerly made soaps only of soft consistency, now yield the more valuable hard soaps. This has led to a very rapid development of the art with respect to the production of soap making fats. In particular fish and whale oils have been made use of, because these oils may be completely deodorized by the addition of hydrogen.

According to Tsujimoto, the odor of fish oil is due almost entirely to a fatty constituent and not to so-called impurities. This fatty constituent is clupanodonic acid, having the formula, $C_{18}H_{28}O_2$, which, therefore, by the addition of 8 hydrogen atoms becomes stearic acid. When hydrogenated down to an iodine number of about 50, fish oil has the consistency of hard tallow and the odor of fish oil is wholly absent. Even the fishy taste is then scarcely in evidence.

For soap making this product is satisfactory as it complies with the test for a deodorized fish oil suitable for soap making in that the odor of the original oil is not apparent when laundried goods on which such soaps are used are ironed. If, however, the hydrogenation is not carried on to a point where the iodine number is approximately 50 or less, there is some danger that the fishy odor will become apparent during the ironing operation.

Hardened linseed oil has met with favor as a soap makers' fat. Ordinary linseed oil is unsuitable for preparing toilet soaps as the saponified product discolors in a short time. The hydrogenated oil is not open to this objection.

Hydrogenation Practice. The following general procedure may be laid down for guidance in the equipment and operation of a hydrogenating plant, irrespective of the character of the oil employed.

The starting point is the preparation of catalyzer. Of course the procedure employed for its preparation depends on the type of catalyzer selected.[1] Suppose nickel be chosen as the active material, to be used on a suitable carrier or supporting base. To this end a solution of a nickel salt such as the nitrate or sulphate is mixed in vats with the support, in the presence of a precipitant, or the latter is subsequently added, and the material is well agitated. Soluble salts may then be removed by washing and the material dried. These operations may take place in a

[1] Several patents have been taken out on catalyzers of different kinds adapted for oil hardening.

filter press supplied with air under pressure. The caked product should be ground in a ball or pebble mill until resolved into a fine powder.

The catalyzer is now ready for reduction, which should be performed with extreme care as the entire oil hardening process depends on the efficiency of the catalyzer. A simple type of catalyzer reducing device is represented by Fig. 297. *A* is a brick structure which contains the reducing drum *B*. The latter is rotated by means of the sprocket *C*. E^1E^2 are stuffing boxes which admit of rotating the drum without disturbing the gas inlet and outlet. The catalyzer is admitted and withdrawn through the gate *G*. The drum is filled about two-fifths full of the catalyzer and hydrogen passed in. When a test for oxygen shows that all the air has been expelled the drum is heated to a temperature not exceeding 360° C. During reduction the hydrogen is passed through at a considerable rate in order to remove the steam formed thus reducing the partial pressure of the latter and facilitating the reduction of the nickel oxide or hydrate. The gases issuing from the exit side of the drum may pass through a water seal and after purification, may be returned to the gas holders to be used again. When the issuing gases are found to contain no steam the reduction is complete, the heating is discontinued and the catalyzer allowed to cool in a current of hydrogen.

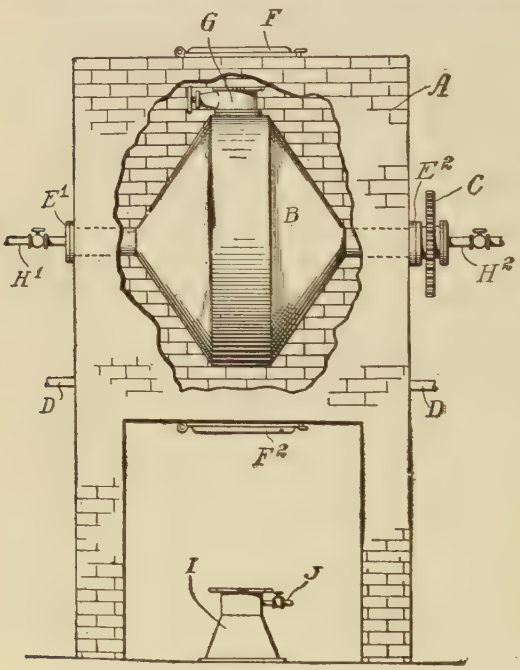


FIG. 297.

After cooling the catalyzer, the hopper I is coupled to the flange of the gate *G*. The bottom of the hopper dips below the surface of oil contained in a receptacle beneath. Hydrogen is passed in at the valve *J* and the air expelled from the hopper. The valve of the reducing drum is now opened and the catalyzer allowed to fall into the oil with which it should be thoroughly mixed. Thus the catalyzer is effectively sealed from the air.

This method of abstracting catalyzer from the reducing drum prevents oxidation of the nickel which occurs to a greater or less extent when the catalyzer is withdrawn in contact with the air.

Another method of preparing catalyzer is to heat nickel carbonate, hydrate, formate, acetate, etc., in fatty oil to a temperature of 240–260° C., usually in the presence of hydrogen as a reducing gas. An effective finely divided catalyzer is obtained in this manner.

The catalyzer-in-oil may then be transferred to a large agitating tank in which oil is added in sufficient quantity to make the mixture contain the correct percentage of catalyzer. The contents are thoroughly agitated and transferred to the hydrogenator or converter, where the actual hydrogenation takes place.

Tall iron tanks may be used for this purpose, one type of which is shown in Fig. 298. The air in the hydrogenator is displaced by means of hydrogen and the mixture of catalyzer and oil pumped from the agitator *A* into the hydrogenator *C*. The contents of the hydro-

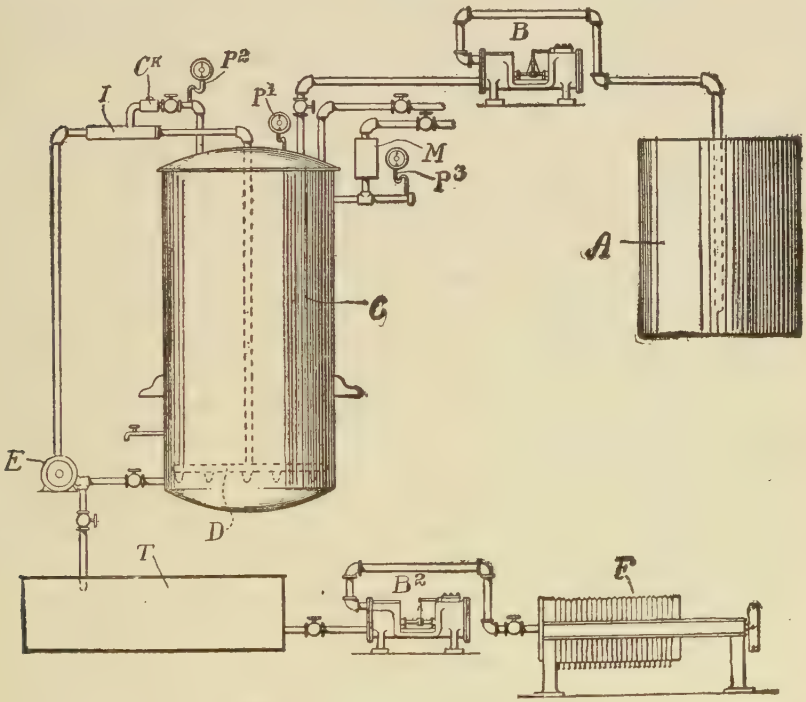


Fig. 298.

genator are heated to a temperature of 175–190° C. by means of superheated steam or hot oil coils, the latter being preferable owing to the danger of leakages of steam into the chamber. The temperature of the contents of the hydrogenator should be registered by means of a reliable thermometer, preferably a recording pyrometer.

The oil and catalyzer in the hydrogenator are circulated by means

of the rotary pump E which takes the liquid from the bottom of the hydrogenator and pumps it through the inductor I where hydrogen drawn from the gas space at the top of the hydrogenator is mixed with the oil. CK is a check valve to prevent oil from entering the tank through the suction tube in the event of the inductor suction nozzle becoming flooded. The mixture of oil, catalyzer and hydrogen is ejected through the distributor D at the bottom of the hydrogenator.

The hydrogen inlet is provided with a safety device M and a pressure gage P_3.

The pressure maintained in the hydrogenator is variable according to the oil under treatment and may range from atmospheric or less up to about 25 pounds.[1] The difference in the readings of the pressure gages P_1P_2 registers the suction of hydrogen at the suction nozzle of the inductor. Samples of oil may be withdrawn from time to time by means of a sampling cock. When the sample indicates that the oil has the required hardness the hydrogenator is emptied through the bottom outlet and the contents run into large tanks T which are heated by means of steam coils. From these tanks the mixture of oil and catalyzer is pumped into filter presses where the catalyzer is removed. The oil is finally run into cooling tanks where it solidifies to a hard fat ready to be made into lard compound, soap or other product.

The transformation to olein of the glycerides of linoleic and linolenic acids or other highly unsaturated acids usually does not result in any appreciable change in the titre. As these bodies generally are to a considerable extent transformed into olein before olein becomes stearine, hydrogen will be absorbed by the oil without hardening, to a degree dependant on the proportion of these highly unsaturated bodies present. Often an hour or more is needed to bring an oil to the olein stage, after which hardening will progress rapidly.

Of course, the method given above is capable of many modifications as oils of different character require different treatment and in consequence often times call for equipment which varies considerably from that given by way of illustration. Catalyzers vary a good deal in their properties and conditions which are suitable for nickel in some of its forms will not answer for palladium. A much lower temperature usually suffices when using the latter metal as a catalytic substance.

A simple type of converter now extensively used is shown in Fig. 299. It consists of a closed tank equipped with a steam coil and stirrer. The vessel is charged with oil and catalyzer and the charge is heated to the requisite temperature when hydrogen is introduced by the small pipes in the bottom of the apparatus. The oil is stirred vigorously dur-

[1] One of the difficulties met with in the handling of hydrogen has been the loss by leakage of the gas. Under pressure and at a temperature of 150° or 200° C., hydrogen is surprisingly penetrating. Autoclaves with welded seams are desirable for high pressure and high temperature work. Moving parts should be avoided as far as possible.

ing the operation. Heat is developed in hydrogenating fatty oils and when a considerable quantity of oil is being hardened, the heat of reaction may be not only sufficient to maintain the batch at the reacting temperature but may even cause the temperature to rise too high, so that cooling is needed. This is especially noticeable with freshly prepared catalyzer. Sometimes preliminary heating by steam to 100–120° C. suffices to start the reaction and the temperature rises rapidly. At 170–180° C. water may be passed through the coil to prevent overheating.

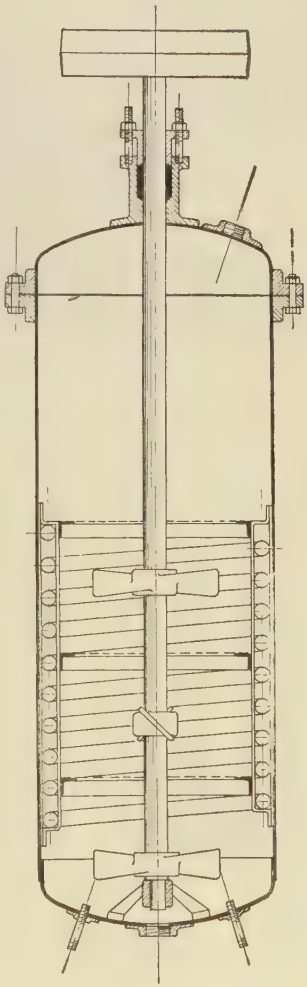


Fig. 299.

(For a detailed description of hydrogenating processes see Ellis, " The Hydrogenation of Oils." Second Edition, 1919. Van Nostrand Co., N. Y.

Edible Hydrogenated Oils. Since the addition of less than 1 per cent of hydrogen suffices to convert cottonseed oil or other vegetable oils into a fatty body of at least the consistency of lard, it follows that manufacturers of ordinary lard compound (that is to say, a mixture of about 85 to 90 per cent of refined cottonseed oil and 10 to 15 per cent or so of oleo-stearine) have promptly turned their attention to the production of compound by a "self-thickened" cottonseed oil.

The high cost of oleo-stearine prevailing during recent years makes the method an attractive one and the hydrogenated product from cotton seed oil, if properly made, is stable in character. Unquestionably, also, the hardening process is destined to increase the demand for cottonseed oil in the manufacture of edible fats.[1]

By the hydrogenation process a lard substitute may be prepared in two ways. The entire oil may be simply hardened to the consistency of lard; care being taken to employ an oil as nearly neutral as possible to prevent excessive solution of catalytic metal, and to avoid a high temperature of treatment so as not to impair the flavor of the product. If the color and flavor are detrimentally affected, resort may be had to a further treatment with fu ler's earth followed by steam vacuum deodorization. The addition of a small amount of cocoanut oil benefits the flavor.

[1] In 1916, the sales of a hydrogenated oil product known as " Crisco " amounted to over 60,000,000 pounds.

The other method is that of making lard compound which as indicated above involves thickening a large proportion of normal oil with a small

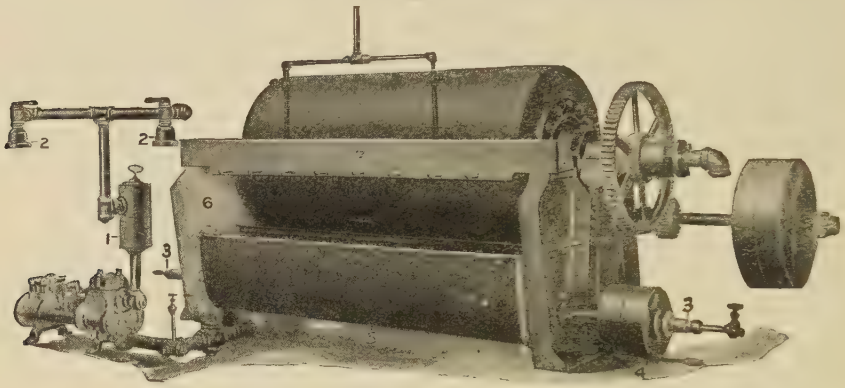
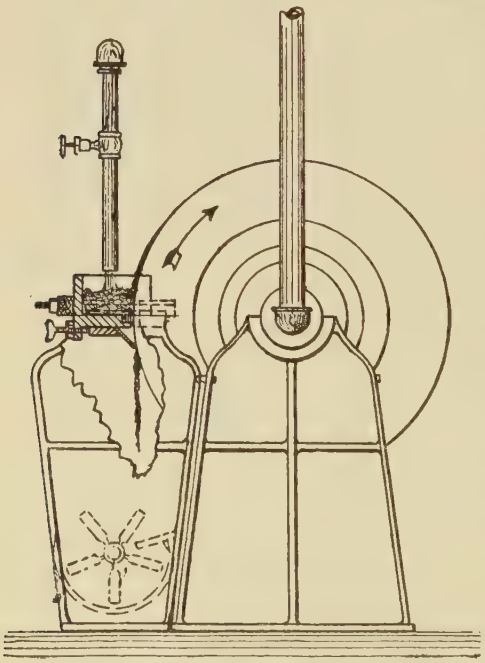


Fig. 300.

amount of a relatively hard hydrogenated product. This may be carried out as follows: After the oil has been hardened, it is freed of catalyzer and then may be run into tanks containing the requisite amount of deodorized cotton oil (or other edible oil) and if necessary the mixture further clarified and filter pressed. With hardened cotton oil of 58–60 titer, only 7–10 per cent is required to thicken the oil to the consistency of lard, although in hot climates a somewhat larger proportion may be needed. The mixture is run onto a chill roll to cause rapid solidification and after slight aeration to improve the color is ready to be packaged. Fig. 300 shows a chill roll or lard cooler of the type usually employed.



END VIEW.
Fig. 301.

In this illustration the large upper cylinder or roll is chilled by the circulation of brine and is slowly rotated, say from 6 to 10 R.P.M. The hot liquid compound at a temperature of 50–55° C. is run into the feeding trough 7 and falls onto the chilling

roll forming a thin, somewhat translucent film which quickly cools and solidifies. The solid fat is removed by a scraper and falls into a picker trough 5. The latter contains a shaft equipped with beating and conveying blades which churn the composition and destroy the translucency, producing an opaque white product of lard-like appearance. The picker is run at a relatively high speed, say 175 to 180 R.P.M. Fig. 301 is an end view showing chill roll, feeding trough and picker. In Fig. 302 the cooler and picker appear on the left hand, in the center is a pump which withdraws the product from the picker and forces it through the pipe line to the packaging cocks on the right hand. Too high a speed of

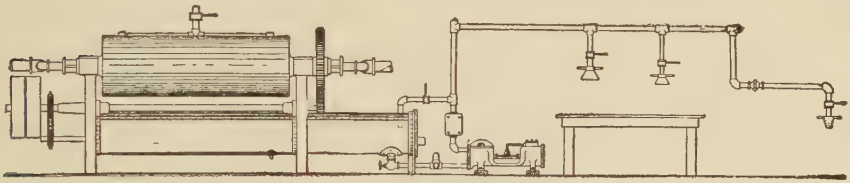


Fig. 302.

the picker blades incorporates an excessive amount of air in the product rendering it "fluffy."

The speed of rotation of the chilling roll is governed by the rate of feed and temperature of the brine. The latter may be kept between, for example, -5 to $+10°$ F. for good results. If the brine is too cold, the product is liable to drop badly from the roll and the texture is not always satisfactory. This, however, may be largely remedied by increasing the feed. In winter the brine may be held at a slightly higher temperature to prevent brittleness. In the hottest weather, very cold brine should be used to aid in securing a product which will preserve its color and consistency for a considerable time.

When properly made the compound derived by the hydrogenated oil thickener is excellent in color, texture, flavor and keeping qualities. By many it is considered superior in several respects to oleo-stearine compound.

Possibly, however, for best results as to stability it is desirable to hydrogenate the entire body of oil to a fatty acid titer of 36 or 38, or whatever consistency may be required, rather than to take a relatively small proportion of the oil and harden it to a titer of 50 60 or thereabouts and incorporate with unhydrogenated oil. It appears that the hydrogenation of the total body of the oil, by transforming the linoleic and linolenic compounds and the like, has a tendency to improve the oil as regards its edibility and certainly gives it greater stability. The flavor of lard compound is, however, preferred by many large users of lard

substitute presumably because of the proportion of normal oil which it contains, and the manufacturing cost is lower.

Dry-shortening. Hydrogenated cotton oil of melting-point 58–62° C. may be ground to a powder applicable as a dry-shortening. The powdered fat may be mixed with flour and the dough batch made from this stock. The shortening value of the hard fat is high.

CHAPTER XXVII

LUBRICATING OILS

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Manufacture. The manufacture of the various oils and fats has already been given in Chapters XXII and XXIV. By way of review, it may be said that the petroleum oils, which make up the greater portion of the lubricating oils, are prepared in two ways: by a "cracking" distillation, which produces the bulk of the paraffine oils, or by a distillation in which dry steam is used to lift the heavy oil vapors out of the still. Consequently the latter oils do not require treatment with sulphuric acid to refine them. Both classes of oils may be filtered through bone charcoal or fuller's earth to improve the color; there seems to be a clearly defined impression that the loss of color is also accompanied by a loss in the lubricating value. Acid-treated oils emulsify more readily with water, and partly on account of the "sulpho" compounds which they contain are less desirable as lubricants; sulphuric and sulphonic acids are difficult to remove completely.

Besides these two classes of oils, we have those of a **paraffine** base or chiefly C_nH_{2n+2} compounds and those of an **asphalt** base or C_nH_{2n-2}, C_nH_{2n-4} (napthenes) C_nH_{2n} compounds. The asphaltic base oils are about 7° Baumé heavier, flash lower, and are much more viscous than the corresponding paraffine base oils; they also lose their viscosity more rapidly except at high temperatures, when the reverse holds true. Consequently when these oils are specified, their viscosity should be from 25 to 50, or in some cases even 75 per cent greater. The specifications throughout this chapter refer to the paraffine base oils.

General Considerations. The object of lubrication is to diminish friction and thus conserve power. The shaft does not (or should not) come in contact with its box, but revolves on a thin film of lubricant. I like the conception of Southwick that the shaft rotates on the molecules of the oil as it were upon the balls of a ball bearing. The resistance which the particles of this film offer to being torn apart, or the shearing modulus, as the engineer terms it, measures the efficiency of the lubricant employed, consequently the cardinal principle underlying all lubrication is to *use the thinnest (or least viscous) oil that will stay in place*

and do the work. Obviously, then, the viscosity or "body" of the oil is of the greatest importance in choosing an oil: this should not be taken at any arbitrary temperature, 70°, 100°, or 212° F., but at the temperature, or between the temperatures, *at which the oil is used.* It often happens that one oil is less viscous than another at one of these temperatures and at the temperature of use the reverse is the case, consequently the other oil should be chosen, in accordance with the principle given above.

Another important consideration to be observed in choosing a lubricant is, that it should not absorb oxygen from the air, forming a gum which would increase the viscosity, or turn rancid, and attack the metals with which it is brought in contact. The liability to oxidize or gum can be shown by the gumming test, which also has been found to be a measure of the extent to which an oil will carbonize in a gas or gasoline-engine cylinder. Besides these two tests, which may be considered as measuring the efficiency of the oil, other tests are employed which either measure the safety, serve to identify the oil, or to determine if it be suitable for the purpose for which it is intended. Such are the flash and fire tests, the evaporation test, the free acid test, and the test for thickeners or soap; while the specific gravity of a mineral oil, iodine, Maumené and saponification values of an organic oil serve either to identify it or indicate if it be adulterated. The cold test and friction test show its availability under conditions approximating that of use.

Tests,—Rapid Tests:—Heat Test. Heat 20–25 cc. of the oil in a flask nearly to the flashing point and keep it at this temperature for 15 minutes; a satisfactory oil will darken, but remain clear even after standing a day. A poorly refined oil changes to jet black, and forms a carbon-like precipitate, in consequence of the "sulpho" compound previously mentioned.

Emulsification Test. This shows the extent to which an oil will emulsify with water and should be conducted together with a known oil as a means of comparison. The oil is thoroughly shaken or stirred together with an equal volume of distilled water and allowed to settle for a day. If "sulpho" compounds be present in the oil, they cause it to mix with the water, forming a milky suspension with curds in it; a good oil shows a clear, well defined line between the oil and water, with little or no turbidity. The results of this test should coincide with those of the heat test and will usually show an "acid-treated" oil; a filtered oil emulsifies less than a "red" oil.

Gasolene Test. This is preformed by dissolving the oil in the gasolene (from Pennsylvania crude) and noting the amount of precipitate or tar produced. It indicates adulteration with heavy asphaltic oils or tarry still residues.

The other tests to be made will naturally vary according to the use for which the oil is intended. The viscosity and gumming tests are of cardinal importance, and should be applied to all lubricating oils; if the oil is to be used indoors, the flash, fire and evaporation tests should

be applied, as they measure the fire risk; the cold test indicates the availability of the oil at the working temperature; the emulsification test shows the behavior of the oil when in contact with water, in the crank case or turbine; the gasolene test shows the heat treatment of the oil or its adulteration with "still bottoms"; the gravity indicates the base of an oil—whether paraffine or asphaltic, and the iodine, Maumené and saponification tests serve usually to identify the organic oils.

Viscosity. This term represents the degree of fluidity of an oil or its internal friction. It is independent of the specific gravity of the oil although this in pipette instruments influences the time of efflux. Within certain limits it may be taken as the measure of the value of an oil as a lubricant, by comparing the viscosity of the oil under examination with that of other oils which have been found to give good results in practice. It is usually determined by noting the time in seconds required for a certain quantity of oil, 60 cc., to flow through an orifice at a certain temperature. The Saybolt Universal Viscosimeter is the instrument generally used by the oil trade, although the Engler has been adopted by certain U. S. Government bureaus. For greases and lumpy solutions the Doolittle Torsion or MacMichael viscosimeter is recommended.

Gumming Test. This test gives an idea of the amount of change that may be expected in a mineral oil when in use. The resinified products formed increase the friction of the revolving or rubbing surfaces. It is also a measure of the amount that an oil will carbonize in a gasolene cylinder. It depends upon the amount of change or tarry matter produced in the oil by mixing it with nitrosulphuric acid.

Flash and Fire Test. The flash test is the lowest temperature to which the oil must be heated to give off vapors in sufficient quantity, which, when mixed with air, produce an explosive mixture. This temperature in the case of a lubricating oil should not be below 300° F. The fire test is the lowest temperature at which it will give off vapors which when ignited will burn continuously.

The test is made by heating the oil at a definite rate either in the Cleveland (open cup) tester or in the Pensky-Martin (closed cup) tester. The latter gives the more concordant and also the lower result.

Evaporation Test. The evaporation test shows the quantity of oily vapor an oil will give off at the average temperature of the bearing; this quantity should not exceed 5 per cent, and is of importance in two ways. It represents the amount of oil serving its purpose, and of oily vapor affecting the fire risk.

Free Acid Test. The free acid test shows, as its name denotes, the amount of uncombined acid contained in the oil: this in the case of mineral oils is sulphuric, coming from the refining process; with the organic oils it is an indication of age or rancidity and is usually oleic. There should be no free sulphuric acid, although some authorities say it must not exceed 0.3 per cent, calculated as SO_3. Others say that

the combined sulphur must not exceed this quantity; the permissible amount of oleic acid varies according to the purpose for which the oil is to be used; for tallow for cylinder oils not more than 0.15 per cent, for prime lard for signal oil not more than 0.2, and for extra No. 1 lard not more than 1.5 per cent. Free acid in oil attacks the metals of the bearings, journals, cylinders, and containers, and in the case of signal oils chars the wick so that the flame is extinguished sooner than it should be.

Soap Test. Test for "oil pulp," or soap: To artificially and temporarily increase the viscosity of oils—in order to pass specifications—recourse is had to the addition of a small percentage of "dope," "oil thickener," or "white gelatine," a soap, usually oleate of aluminium. This greatly increases the viscosity,[1] causes the oil to chill more easily and to emulsify, thus increasing the friction. Furthermore, it is precipitated by contact with water or steam, causing clogging of the machinery.

Specific Gravity. The specific gravity of an oil when stated as a decimal indicates the usual relation to water; this is commonly employed with the organic oils; the gravity of the mineral oils is expressed in degrees of the Baumé scale for liquids lighter than water; here water is 10°, engine oil, for example, may be 26°, spindle oil 35°, kerosene 47°, stove gasolene 62°, illuminating gasolene 86°; it is to be noted that the lighter the oil the larger number on the Baumé scale. These degrees have no connection with the flash-point, fire-point, or boiling-point of the oils.

Iodine Number. The iodine number or value represents the per cent of iodine absorbed by the oil under fixed and precise conditions: this is quite a definite characteristic of oils, although the very fact they are of organic origin means that the vegetable oils are subject to changing seasons and the animal oils to change in feed. In the case of olive oil the variation in the iodine number is from 77 to 88; it is impossible, therefore, to express the adulteration of olive oil more closely than about 5 per cent.

Maumené Test, or the heating test with sulphuric acid, is one of the most important tests to determine the variety or kind of an oil: it possesses the advantage that it requires no complicated apparatus and is simple in execution. It depends upon the principle that when oils are mixed with sulphuric acid, heat is produced and the quantity of heat so produced is characteristic of the various oils. The results are usually reported as the rise of temperature in degrees centigrade obtained when 10 cc. of acid is mixed with 50 grams of oil.

Saponification Value. The saponification value indicates the number of milligrams of potassium hydrate required to saponify one gram of oil; as this for most of the oils is about 193 it is no criterion by which to distinguish one oil from another. Its chief value is to determine if an

[1] In a case which came to the writer's notice, the oil would not flow from the viscosimeter at 70° F., required 1167 seconds at 85° and 181 seconds at 110°.

organic oil be adulterated, or compounded with an unsaponifiable one, as mineral or rosin oil. This is done by dividing the saponification value obtained by 193; the quotient represents approximately the per cent of organic oil.

Cold Test. The cold test is the temperature at which the oil will just flow and indicates the availability of the oil at this temperature. Cases are on record of the stalling of railroad trains and the setting fire to the factories owing to the oil freezing in the journal boxes.

Friction Test. The friction test measures the power consumed by the oil. This is carried out upon a bearing as nearly perfect as can be made by mechanical skill and under what may be called ideal conditions —regularity of feed, temperature, and pressure. In performing this test, it should be remembered that the effects of the oil previously used upon the machine persist for about eight hours, even though the shaft and bearing be chemically clean. Consequently reliable readings cannot be obtained until after the machine has run at least this length of time with the oil to be tested.

Choice of Oils for Certain Purposes. R. H. Thurston said, "I have learned not to dogmatize about oils; the only thing to do in any case is to test them and see just what they are good for." By "test" he meant either a friction test or "practical" test. While this is of course true, yet the former is tedious and the latter may involve too much risk, and equally good results for practical purposes can almost always be obtained by the use of brief physical and chemical tests such as viscosity, flash, and specific gravity. Practically the only case where these constants do not hold is where the oil is emulsified with water when used, and here the water seems to exercise a decided influence.

The selection of a suitable oil is determined by the pressure on the bearing per unit area—a square inch—and is independent of the size of the bearing; thus it can happen that the same oil can be used both on a large and a small bearing.

From what has already been said, an oil should be sufficiently fluid to flow readily between a journal and its bearing at the temperature of use, and not be forced out by the pressure under which it is running or to which it is likely to be exposed; any viscosity in excess of this means a needless waste of power. (Apply the viscosity test.)

The fact should not be overlooked that mineral oils lose their viscosity rapidly when heated, more so than the organic oils, and that the tendency of the latter is to increase the viscosity.

A suitable lubricating oil should not gum or thicken on exposure to the air (gumming test); it should not give off inflammable vapors below 300° F. (flash test); nor lose more than 4 per cent on exposure for a working day at the temperature of the bearing upon which it is used (evaporation test). It should contain no acid to attack the bearing or shaft (free acid test). It should have the least possible cohesion among

its own particles and the greatest possible adhesion to the metals of which the shafts and bearings are composed. Petroleum oils fulfill the first condition and animal or vegetable oils the last.

In addition to the conditions just outlined, the way and manner in which the oil is applied or the "feed" influences the choice. The various feeds may be divided into forced, gravity, ring or wick, splash, flooded bearing and hand feed, or combinations of these. Of these the forced, gravity, and ring or wick, are economical, of high efficiency, collect little dirt, and in the case of two first, furnish strained oil and use a light or medium-bodied oil; the same holds true of the flooded bearing except as regards the efficiency in the recovery of the oil. The chief disadvantage of the splash feed is that any dirt and wear from the bearings are not separated from the oil. Hand feeding is most wasteful and inefficient, depending upon the efficiency of the individual. Forced feed is employed with high speeds and bearing pressures; it uses a somewhat more viscous oil, particularly with automobiles than the other types of feed.

Wear and Tear of Oils. The question is often asked as to whether oils "wear out"; this continues the Southwick conception of the ball bearing and implies that the balls or molecules break or wear out. Carpenter and Sawdon showed that the gravity and viscosity of oils in circulating systems increased, but the actual friction test was slightly lower at low pressures, and a trifle higher at high pressures. With automobile lubrication the dilution of the oil by the gasolene residues cause it to become thinner; consequently fresh oil should be added to a circulating system to keep the viscosity practically constant.

Air Compressor Oils. The oil should have a low evaporation test and a flash-point at least 100° F. higher than the highest temperature likely to occur in the cylinders. A filtered oil should be used, and for pressures up to 125 pounds per square inch it should have a viscosity of 270 seconds at 100° F. for higher pressures an oil of 320 seconds or higher at 100° F. should be used.

Automobile or Gas Engine Oils. Gas engine oils, particularly for the cylinders, should possess as their chief requisite, besides that of lubrication, the property of not carbonizing at the temperatures attained. The liability of carbonization seems to be intimately connected with the amount of tarry matter yielded in the gumming test and residue in the carbon residue test. For automobiles the oils of the following characteristics have yielded good results. Flash 400–470°, viscosity 180–185 seconds (at 100° F., Saybolt Universal) gumming tests very slight or slight. For large size gas engines probably a heavier oil would be required having these characteristics;[1] gravity 26–28° Bé., flash 400–475° F., viscosity 250 seconds at 70° F. or at 100° F.

Belt Oils or Dressings. Where the object is the softening of the belt they are usually mixtures of solid fat, waxes, degras, or tallow with fish

[1] Davis, "Friction and Lubrication," p. 121.

oils to make the belts cling; in some cases they are mixtures either of corn or cotton-seed oils, which have been treated with sulphur chloride, with mineral oil and thinned with naphtha, or they may be mixtures of the above fats with rosin or rosin oil. These are least desirable. Preparations containing wood tar are also used.

Car Oils, Reduced Oils, Well Oil, Black Oils. These are commonly crude oils from which the more volatile portions, the naphthas, and, burning oils, have been removed by distillation. Some railroad specifications require a gravity of 29° Bé., flash-point 280–300° F., cold test 10–32° F., according to the season of use, and a viscosity 160 to 220 seconds at 130° F. The lower figures refer to the "summer," the higher to the "winter" oils.

Ice-machine Oils. These are light spindle oils of a gravity of 26–27° Bé. 60 to 100 seconds at 70° F., viscosity 325–360° F., flash, and a cold test of 0 to 4° F.

Crank-case Oils. These should emulsify but little with water, consequently should be pure filtered mineral oils and not acid-treated oils. Much seems to depend upon the water with which the oil is mixed in the crank case, so it is difficult to predict how oils of practically the same constants will behave with different waters. An oil giving these figures has proved eminently satisfactory: gravity 26–27° Bé., flash 455° F., viscosity 100 seconds at 212° F.

Cylinder Oils. Cylinder oils, or more accurately, steam cylinder oils, as the Germans call them, are divided into low and high pressure. Here a different problem has to be met, that of making the oil adhere to the surfaces of the piston and valves. This is accomplished by the addition of some fatty oil which adheres to the metals and the mineral oil adheres to it. The action of the fatty oils would seem to be analogous to that of a mordant in fixing dyes. Pure fatty oils, while they have been, and may now in some cases (with low pressures) be used, are open to the objection that these, being glycerides, are decomposed by high-pressure steam with the liberation of fatty acids which attack the iron of the cylinder, causing pitting and scoring.

$$C_3H_5(St)_3+3H_2O=C_3H_5(OH)_3+3HSt.^1$$

On the other hand, when the condensed water from the exhaust steam is used as boiler-feed water, owing to the fact that these fatty oils emulsify so well with it, renders it necessary to use pure mineral oils. The cylinder stocks, that is, the pure petroleum bases, have the following characteristics. Gravity 23 28° Bé., flash 500–630° F. viscosity 160–230 seconds at 212° F. It would seem hardly necessary to state that the low-pressure oil should have the lower of these figures. The viscosity of cylinder oils should be taken at the temperature corresponding to the

[1] St = Stearic acid = $C_{17}H_{35}COOH$.

pressure at which they are to be used. For superheated steam the following figures are given for the oil to be used: flash-point 625–640° F., viscosity 315–325 seconds at 212° F.

The fatty oils used are, degras, tallow, linseed, cottonseed, and blown rape, all as free from acid as possible and in quantities varying from 1 to 25 per cent; the wetter the steam the larger the amount of compounding.

Engine Oils. Engine oils are classed as light and heavy; besides being used for engines, as their name denotes they find general employment for shafting, machinery, etc., about the mill or works. They are usually hydrocarbon oils of gravity 32–23°, flash 300–430° F., and viscosity from 50–400 seconds at 70° F. Where the duty is heavy or the bearings are rough, they are sometimes mixed with animal oils, as lard or whale oils.

A heavy oil has a viscosity of 280–340 seconds at 100° F.; medium is 175–200 seconds, and light 50–150 seconds at 100° F.

For Diesel engines[1] special oils are required as follows: for high-speed marine engines, a neutral filtered oil of 150 seconds viscosity at 100° F.; for heavier engines, a filtered cylinder stock of 150 seconds viscosity at 212° F., for heavy and slow-speed engines, an oil of 450 seconds viscosity at 100° F.

Greases. Gillett[2] divides the greases into six classes:

1. The tallow type, a mixture of tallow with palm-oil soap with some mineral oil; this was common twenty years ago.

2. The soap-thickened mineral-oil type, a mixture of mineral oil, usually with lime or sometimes soda soaps, the commonest type at present.

3. Types 1 or 2 mixed with graphite, talc, or mica.

4. The rosin-oil type, a mixture of rosin oil thickened with lime, or sometimes litharge, with mineral oil. They contain often 20 to 30 per cent of water and are used as gear greases. They may contain also tar, pitch, ground wood, or cork, and any of the fillers mentioned in 3.

5. Non-fluid oils: oils or thin greases stiffened with "oil pulp" or "dope," i.e., aluminium oleate.

6. Special greases with special fillers.

These greases show a high coefficient of friction at first, causing a rise of temperature which melts the grease, producing the effect of an oil-lubricated bearing. The graphite greases show an unexpectedly low lubricating power; the rosin greases show a high friction at first, but after the bearing has warmed up compare well with the more expensive greases. The high moisture content would seem to have the advantage of making them less sticky. The lime soap greases (Class 2) are not as good as the tallow greases (Class 1), and are inferior as lubricants to those compounded with soda soaps.

[1] Battle, "Lubricating Engineer's Handbook," p. 197.

[2] *Jour. Ind. and Chem.*, I, 351.

By choosing the materials, soft or hard soaps, and light, medium or heavy oils, or solid greases, with suitable fillers talc or graphite, and varying their proportions, greases can be made in any desired consistency, from the semi-fluid oil to the hot neck grease.

Greases are in many cases to be preferred to oils, particularly where oil spots from the bearings are to be avoided. They are used upon dynamos, shafting, gears, and where heavy pressure is applied, as in the trains of rolls in rolling mills.

Some of these greases have received special names, as fiber grease, gear or pinion grease, graphite grease, petroleum grease, and hot neck grease.

Fiber grease is so called because it appears to be fibrous, especially when pulled apart; it is an anhydrous soda or potash soap (Class 1) mixed with mineral oil. *Gear grease* is usually a mixture of fiber grease with mineral oil, or it may contain rosin oil (Class 4). *Pinion grease* is commonly made from petroleum residuum (still bottoms); pine tar is often added, and in some cases the grease consists solely of this tar to the detriment of its lubricating qualities.

Graphite grease is a mixture of about one part graphite and two parts gear grease; it is especially useful in wet places, as it is not easily washed out of the bearings, particularly if it be compounded with a lime soap. *Petroleum grease* is a heavy vaseline-like body obtained from still residues (Chapter XXII) after the cylinder oil has been distilled off. *Hot neck grease* is the stiffest of all the greases; it is usually a stearine or wool grease pitch, or petroleum residuum mixed with rosin, talc and graphite.

The following tests are usually applied to the greases: flash, free acid, dropping-point, soap content, free oil or fat saponifiable and mineral, free lime, fillers, and water.

For the flash-point a 50 cc. porcelain crucible is used; the free acid is determined as with the oils; the dropping-point, according to Ubbelohde's method, by noting the temperature at which drops fall from a tube of grease surrounding the thermometer and having a standard orifice at the bottom. The soap content is most readily determined by ashing the grease and applying the usual quantitative methods to the ash. The free oil or fat is determined by extraction with gasolene, or if lime soaps be present, with ethyl acetate at room temperature; the oils extracted are examined as described under oils; the free lime and fillers are determined by the usual quantitative methods. Water is best determined by distilling with xylol according to Marcusson.[1] The table on the following page shows the composition of some of the greases.

Grease or "cup grease" should be homogeneous, and contain at least 80 per cent mineral oil of 24–28° Bé.; it should be neutral—containing neither free alkali nor fatty acids, nor should it contain grit nor useless filler, as paraffin wax. The ash should not exceed 2.75 per cent, and the loss on evaporation for an hour at 110° should not exceed 3 per cent.

[1] Mitt. k. Materialsprüfungsamt, **24**, 48.

COMPOSITION OF SOME GREASES *

Name.	Flash-point, ° C.	Melting-point, ° C.	Consistence, Gms., 20° C.	Water.	Ca Soap.	Filler.	Mineral Oil.	Fatty Oil.	Free Acid.	Coefficient Friction.
Graphite	195	93	18	tr.	11	16	56	17	0	.097
Sum. motor	160	87	170	tr.	38	...	36.5	25.	tr.	.075
Winter motor	175	86	7	tr.	32	...	40.	37[5]	6.1	.063
K1	193	85	24	0.2	16	...	67.	16.	0	.057
K2	195	93	66	0.3	20	...	60.	20.	0.3	.054
Auto	190	79	11	1.0	19	...	60.	20.	tr.	.046
Tallow	210	52	150†	2.5	...	1.4[1] 2.1[1]	22.	73.5	0	.022
Tallow XX	215	49	200	tr.	...	30.[7]	20.	48.	0	.029
Lead resin oil	240	102	7	24.7	...	1.7[2]	...	0.	0	.067
Lime resin oil	198	77	31	tr.	...	9.9[3]	...	0.	0	.048
Lime resin oil	198	75	4	20.0	...	7.8[3]	...	0.	0	.036
Soda grease	215	83	35	0	...	22.[4]	78.[6]	0.	0	.019
Non-fluid oil	210	76	27	0	9.8	12.9[4]	70.3	7.	0	.026
No. 4 petrolatum	247	47	6	0	....	....	100.	0.	0	.018
Lard oil	265	5	0	0	...	....	0	100.	...	.011

* Gillett, loc. cit. † Estimated. [1] Potash soap.
[2] Lead soap. [3] CaO. [4] Soda soap. [5] Mainly palm oil. [6] Oil of 24.2° Bé. [7] Paraffin.

Marine engine oils have about the following characteristics: gravity 22–24° Bé., viscosity 350–580 seconds at 100° F.; flash 395–470° F. These are usually compounded with as much as 15 per cent of extra No. 1 lard, or 25 per cent of blown rape oil to give them lathering properties in contact with water. Experience has shown that the addition of these organic oils is unnecessary; they are expensive and gum the wick feeds.

Milling Machine or Soluble Oils. These are usually lard, sulphonated oils, or mineral oils held in suspension by soaps or alkalies, as borax-sodium carbonate; the soaps are either ammonium, sodium, or potassium, with oleic, resin, or sulpho fatty acids. They should not appreciably attack the metals and should form a persistent emulsion. The U. S. Navy requirements are that upon twenty-four hours' standing upon polished brass, or copper it must not be turned green. German requirements are that a steel plate, 30 by 30 by 3 mm. should not lose more then 18 mg. in a 1 or 2 per cent solution of the oil after lying for three weeks in it.

Neutral Oil. An oil without " cast " or " bloom," obtained by sunning in shallow tanks. The term was formerly applied to oils of 32–36° Bé., 290–318° F. flash and 47–81 seconds viscosity at 70° F.

At present the term includes " viscous neutrals " of a viscosity above 135 seconds at 100° F. and " non-viscous neutrals " below this figure.

"Oil-dag." This is the term applied by Acheson, the discoverer and maker of carborundum and artificial graphite, to a colloidal suspension of pure deflocculated graphite in oil, so fine that it will go through the finest filter paper. Care must be taken that the oil is free from acid, whether mineral or organic, as this causes a precipitation of the graphite.

Oilless Bearings. These are wooden blocks, often of maple thoroughly impregnated with 35 to 40 per cent of grease, which replace metal journals; the grease may be a mixture of paraffin, myrtle, or beeswax with stearine, tallow or vaseline.

Screw-cutting Oils. These are often mixtures of 26–29° Bé. paraffin, and 25–30 per cent fatty oil, preferably cottonseed, although lard and whale are sometimes used.

Textile Machinery Oils. These are spindle oils, loom oils and the various kinds of engine oils.

Loom Oil. This is merely a heavy spindle oil. One which the writer tested had a gravity of 28°, flash 360° F., and viscosity of 203 seconds, Here, as in the case of spindle oils, the evaporation test should be low, as the hydrocarbon vapors formed have occasioned serious fires.

Spindle Oil. This is the lightest and most fluid of the lubricating oils. The gravity varies from 27–35° Bé., the flash from 320–430° F., the viscosity 30 to 400 seconds Saybolt at 70° F., and the evaporation test should not be over 4 per cent. From what has already been said, nowhere is the necessity for low viscosity greater than in the case of these spindle oils when the bearings are multiplied by thousands. A case is on record where the increase in the viscosity of the spindle oil stopped the engine and shut down the mill. Besides being used for spindles it is used for sewing machines, typewriters, etc.

For bath spindles the viscosity may be 95 to 100 seconds at 100° F.; for open spindles this may be increased to 140 or 150 seconds.

Stainless Oils. These are spindle or loom oils mixed with fatty oils —lard or neatsfoot; the fatty oil, being more easily emulsified or possibly saponified in the scouring process, aids materially in washing out the mineral oil with which it is mixed. One type of these oils is compounded of 40 per cent neutral oil, 30 per cent cottonseed, 20 per cent olive, and 10 per cent first-pressing castor.

Transformer Oils. These should be either pure rosin or mineral oils and be free from water, acid, alkali, and sulphur. They may be freed from the first two impurities by treatment with sodium wire after the usual method of organic chemistry. They should not lose more than 2 per cent when exposed to 190° F. for eight hours, have a viscosity of about 400 seconds at 70° F., a flash of 340–380° F., and remain liquid at 32° F.

Turbine Oil. Steam turbines require a pure filtered non-emulsifiable mineral oil of most excellent quality; as the oil is circulated around the bearings by a pump it should be of low viscosity and gravity and free from

acid, mechanical impurities, and tendency to resinify: it should be low in sulphur contents. An oil of 29–31° Bé., 145–180 seconds viscosity at 100° F., and 390–420° F. flash has given good results.

Watch Oil. For oiling the most delicate machinery as watches (and clocks) the oil obtained from the dolphin, blackfish or " snuffer " is used. This exists in the cavities of the jaw and also in the brain or " melon " of the fish; it is rendered at a low heat, chilled and filtered at a low temperature, bleached and refined by sunning in contact with lead plates to remove acid. It is a pale yellow, very fluid oil of peculiar odor; the viscosity is about 100 seconds at 100° F.

Finally, in making out specifications, certain mechanical details should not be overlooked. The barrels should be clean and the oil should be free from specks, dirt, stearine, glue, or anything likely to clog the lubricators that may be used; the oil should be free from tar (still bottoms) as shown by the gasolene test, and if compounded should be composed of oils that mix perfectly.

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CHAPTER XXVIII

SOAP AND SOAP POWDER

LINCOLN BURROWS

Historical. Before the invention of soap, the ancients employed the juice of certain plants as detergents, and also Fuller's earth. The latter was spread upon the clothes and stamped in with the feet. The art of soapmaking, however, is very old, as is proven by the remains of a soapmaker's shop found in the ruins of Pompeii. Early records show that soap was manufactured in Italy and Spain during the eighth century. The first soap works in France was established at Marseilles in the twelfth century, when olive oil was first employed for the purpose of soapmaking. It was during the fourteenth century that soapmaking is supposed to have been introduced into England.

The methods employed in the early days of the industry were very crude, and it was only when Leblanc introduced his process for the manufacture of soda from common salt that the industry made any advancement. It was Chevreul, however, who raised soapmaking from rule-of-thumb methods to a true scientific industry.

Theory of Soap-making. When tallow, lard, palm oil, corn oil, or other fatty material is treated with a solution of sodium hydroxide or potassium hydroxide, a chemical change takes place, resulting in the formation of a product soluble in water, and possessing properties entirely different from the original oil or fat employed. When the soluble product is treated with an acid the resulting body becomes insoluble. If this operation is conducted in a quantitative manner it will be found that the insoluble substance obtained from the acid treatment is only about 90 per cent of the original weight of the fat. Something, therefore, has been eliminated during the operation. This may be recovered from the acid liquor by evaporation, and is found to possess a sweet taste, an oily consistency, and is known as glycerine. The insoluble portion recovered above has an acid reaction, when combined with alkali is soluble, and upon investigation proves to be made up principally of such compounds as stearic, palmitic, and oleic acids. Thus we draw the conclusion that fats are glycerides of fatty acids; and that in soap-making the caustic alkali decomposes the fatty glycerides with the formation of salts of the fatty acids known as soap, and the separation of glycerine.

In boiled soaps this glycerine is separated, while in half-boiled or cold-made soaps it is not, and remains a part of the soap.
This reaction is indicated in the following equation:

$$\begin{array}{l} C_{17}H_{35}COOCH_2 \\ | \\ C_{17}H_{35}COOCH \\ | \\ C_{17}H_{35}COOCH_2 \end{array} + \begin{array}{l} NaOH \\ \\ NaOH \\ \\ NaOH \end{array} = \begin{array}{l} C_{17}H_{35}COONa \\ \\ C_{17}H_{35}COONa \\ \\ C_{17}H_{35}COONa \end{array} + \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

Glyceryl stearate in tallow — Caustic soda — Sodium stearate (Soap) — Glycerol (Glycerine)

Although there are many substitutes for tallow which are employed in soap-making, they all require caustic for saponification and all act in the manner above described. There are, however, some substances, such as rosin, with which, when used in the production of soap, the action as stated above is modified. Rosin is an acid and unites directly with the caustic soda to make a salt.

Classification of Soaps. Soaps are divided into two principal classes, namely: *hard soaps* and *soft soaps*. In the former caustic soda is employed and in the latter caustic potash is used. The terms *soda soap* and *potash soap* are also sometimes used to distinguish the two classes. Further, depending upon the method of manufacture, we have *boiled soaps, half-boiled soaps*, and *cold-process soaps*. Hard soaps are of various kinds, such as *castile, curd, mottled, yellow*, and *transparent*. Soft soaps come on the market as a paste or in a semi-liquid condition. In some soaps both caustic soda and caustic potash are used in their preparation.

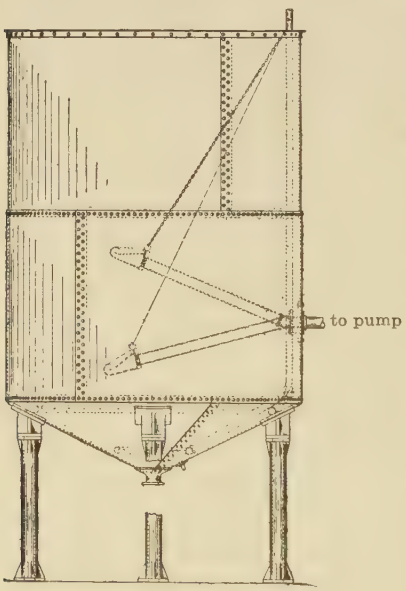

FIG. 303.—Soap Kettle.

As soap is used for a great variety of purposes, its preparation must necessarily vary. The choice of stock depends upon whether a high-grade soap is to be made, in which the choicest materials must be selected, or whether a cheap soap is to be manufactured. Soap is used very largely in the textile and leather industries, and should be specially prepared for the purpose to which it is to be put.

Melting Room. The soap stock, tallow or oil, is received by the soap-maker in tierces or drums and must be melted out of these packages for bulk storage. This is done in a "melting-out" or "steaming-out" room. This room is generally built of wood with an iron sheathing and a floor of iron plates. The room is pitched from the

back to the front so that everything is thoroughly drained out and there is no accumulation. This room is built with partitions so as to make compartments which are just a little larger in width than the drums.

A light track of two rails is laid in the center of each compartment on which the tierces and drums roll easily and in the middle of each track a steam line is laid. At a distance equal to the periphery of a tierce or drum from bung to bung, a valve and short nipple with a swing joint is fitted to the steam line. The steam control is on the outside of the room.

A charge is set by rolling in the packages, blocking them and fitting the nipple, with valve open, into the bung-hole. The steam is turned on after the door of the compartment is closed and the melted tallow or oil runs to a trough or gutter in the front of the room. Where this gutter discharges to the piping which carries the melted fat to the storage tanks, a strainer is provided to keep out large particles, principally bungs from the tierces. After the melting-out is completed, each package as it comes from the room is examined for unmelted fat by means of a small light on an extension cord which is dropped into the bung-hole. The time of melting-out varies with the character of the fat and the outside temperature. It takes quite a little longer in winter than in summer.

Condensed Water in Tallow. After the tallow or oil has been melted it will always contain considerable water from the condensed steam. It is best to dispose of this water as soon as convenient and not allow the fat to stand in contact with it. As soon as the water has settled out it is pumped up into the first kettle to be charged. The clear tallow or oil is then pumped to storage tanks. The change from water to tallow can be caught very readily by the pumpman if a small pet cock is tapped into the discharge end of the pump, by which he can test the discharge from time to time. This freeing of the stock from water is also a means of checking up the weights of any particular lot and serves to keep the registers of the tanks as a true indication of the stock on hand.

Piping. All piping through which tallow or oil passes is fitted with small steaming-out lines and all such lines must be thoroughly steamed-out both before and after any tallow is handled through them. This steaming-out being also carried through the pumps and back to the storage tanks.

Storage Tanks. These tanks are made of iron with loose fitting wooden covers and provided with a large door to admit of frequent cleaning. A closed steam coil is laid in the bottom which keeps the stock above the solidifying point. The drips from these coils are discharged into a small open tank which quickly shows tallow or oil in case of any leak and prevents its loss.

Soap Kettles. Both round, Fig. 303, and square kettles are used for the boiling. They are made of iron, and the soap is heated in a square kettle by a coil laid diagonally across the bottom with arms running to the sides of the kettle. The coil is punched with small holes for the

steam outlet. This serves for agitating as well as heating. A heavy jacket of insulating material is built around the kettle to conserve the heat during the settling.

Boiled Laundry Soap. The melted fat and oil is pumped into the soap kettle from the storage tanks and with it a small stream of 18° caustic soda lye is run in from a separate line. Enough steam is turned on to keep the contents well mixed. The union of the fat and caustic soda sets up quite a little " heat of reaction " and very soon the steam may be eased off. As much boiling room as possible is saved for finishing the saponification. The lye is kept slightly behind the stock until the fat is all pumped up. An excess of caustic can be determined by rubbing a sample taken from the kettle between the fingers until cool; a sharp taste denotes an excess of caustic Toward the end of the saponification, the soap begins to take on a darker color, become smooth and assume a high gloss. A sample taken on a small flat piece of wood, called a paddle, is now quite transparent and rolls off the paddle in sheets. The lye must now be added in small lots with frequent testing as described below. An alkalinity not over .20 per cent is very desirable and a kettle which holds this alkalinity after three boilings and tests may be considered as finished for this change.

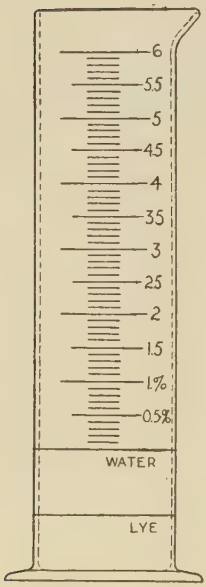

Fig. 304.

Graining. The soap must now be separated from the free glycerine and is done by adding salt in which solution the soap is insoluble. This is called " graining." The kettle is well boiled, dry salt shoveled in or a brine (salt) solution is run in and mixed through by boiling until a sample on a paddle shows the soap in a broad flat curd from which the lye runs freely. The steam is shut off, the soap rising to the top of the kettle and the salt solution containing the glycerine settles out on the bottom.

Testing Alkalinity at the Kettle. A special graduated cylinder (Fig. 304), is used which is marked at 10 cc. Lye, another 20 cc. further up marked Water, and from then on a small graduation at each 2 cc. with a larger mark at each 10 cc. A sample is obtained from the kettle and the lye separated by stirring in enough dry salt to grain out the soap. This lye is run into the graduate up to the Lye mark (10 cc.), water added to the water mark, three drops of phenolphthalein solution put in and then $\frac{N}{8}$ sulphuric acid run in with shaking until the solution is decolorized. Each 2 cc. of acid used equals .10 per cent caustic soda. Percentages are etched at the 10 cc. graduations as .50

per cent, 20 cc.–1.00 per cent, etc. A cylinder large enough to cover 4 per cent will answer about all the needs of the soap-maker. Any man around a soap plant can easily be taught its use and for the rough estimate it is designed for, it meets its purpose.

Second Change. The lye from the first change is drawn off from the bottom into an empty kettle until soap appears and then shut off. The soap is boiled up and a dash of 18° Bé. caustic soda added and after being well boiled through, the alkalinity is tested. If an excess of .20 per cent is not shown, more caustic is run in boiled and tested until the soap holds this alkalinity. Water is now added until the soap shows, after boiling through, a smooth appearance. This is called "*flattening out.*" When the water is all in, the graining is repeated as before.

Amount of Water Added. The amount of water to be added on these "*wash*" changes and the number of these changes to be made depends entirely on local conditions and is usually decided by the time which can be given to its completion and the capacity for evaporation in the glycerine plant. It is usually expressed in per cent on stock saponified as from 200 to 350 per cent, i.e., if 10,000 pounds of fat are saponified, then a lye of from 20,000 to 35,000 pounds are drawn. It is better to make the changes smaller and make five of them than to make only four even if the same volume of water is used.

Rosin Saponification. A straight tallow soap is rather slow in lathering and needs a softening agent such as oil or rosin to increase its solubility. In toilet soaps oil is used and in laundry soap rosin. The rosin is incorporated in two ways, either by direct saponification in the same kettle as the first change was made or by a separate saponification in another kettle and a subsequent incorporation.

Direct Saponification. The first change soap after all the wash changes have been made and last lye drawn is boiled up, a little salt, any scrap or broken soap added and enough 25 to 30° caustic lye run in to "*open*" or grain the soap. While the kettle is slowly boiling, the rosin cracked up in small lumps is shoveled in. From time to time samples taken from the boiling soap are tested for alkalinity and if not up to 2 to 3 per cent, enough caustic is added to bring it up to the mark. While the rosin is being saponified in this way, a "second rosin" lye from another kettle is pumped in and its caustic content assists in dissolving the rosin. An excess of caustic lye must at all times be present in this change as no salt is to be added for graining, the free caustic doing this graining. This is the only lye which is run away to the sewer when settled and it contains nearly all the soluble impurities. When the rosin is all in and the final test for free caustic made, the soap is allowed to settle, generally over night, so as to get out into the lye as much color and impurity as possible.

Saponified Rosin. Water and soda ash (Na_2CO_3) are boiled in a kettle to make a 12° Bé. solution. One thousand pounds of rosin require 150 pounds of ash. The solution is kept slowly boiling while the rosin

is shoveled in, and the solution of the rosin completed by frequent short boilings. It is finished when no more rosin is found floating on the surface after the boiling and settling. Just before it is pumped out of the kettle onto the tallow soap enough dry salt is added to make it pump well. The incorporation with the tallow soap proceeds the same as with the direct rosin saponification except that less caustic soda is used.

Second Rosin Change. When the first lye has been drawn, the soap is brought to a boil and enough 25–30° caustic soda run in to make an

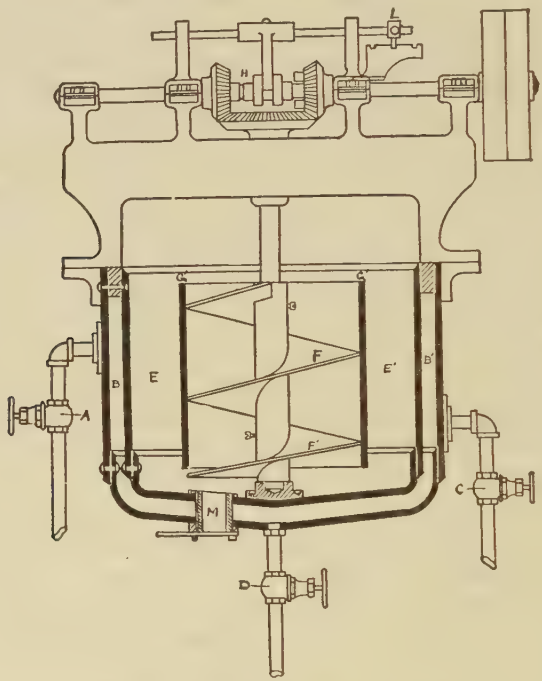

FIG. 305.—Detail of Perfection Crutcher.

A, Inlet for steam; B, Steam jacket surrounding kettle; C, Outlet for escaping steam and condensation; D, slip to jacket; E, space for contents; F, Worm for agitation; G, Case for worm; H, Friction clutch; M, Gate for dumping charge.

alkalinity of 3–4 per cent and continued boiling while a boiled up nigre of a previous boil is pumped in to fill up the kettle. The main object of this change is to insure a complete saponification of the rosin.

Strong Change. When the second rosin lye is off, the soap is boiled up and enough water or 4–5° caustic lye is added to smooth or flatten out the soap and get it into a condition to drop or settle out the excess caustic with the other alkaline impurities ($Na_2CO_3 + Na_2SO_4$).

Finish. After a few hours, the soap will drop a heavy, slimy lye which is drawn off and the soap boiled up. Experience alone now dictates the procedure. If the soap is thick (heavy), a little water is run in it and boiled

through, which leaves the soap as it boils in a smooth, high-polished condition, and when the steam is shut off the process of settling or clarification can readily be seen at once on the surface.

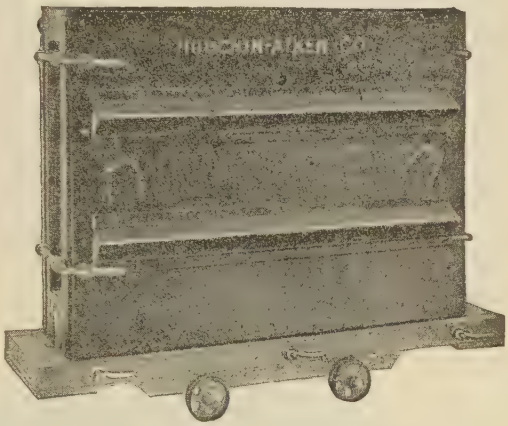

Fig. 306.—Soap Frame.

Settling. The soap should stand about a week to be well settled. During the settling the soap separates into two layers, the upper part being the good soap, i.e., a soap containing but traces or a small amount of free alkali and about 31–32 per cent of water, which seems to be the amount of water needed to make a good settled soap, a sort of water of constitution, and a lower layer or "*nigre*" which is a soap with a large amount (55–70 per cent) of water, free alkali and any other alkaline impurities (Na_2SO_4+NaCl) present. The purpose of the last change is to manipulate the soap, so as to concentrate these impurities in the nigre.

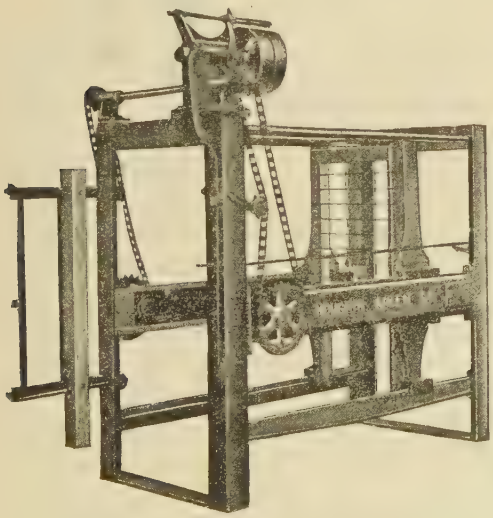

Fig. 307.—Slabber.

Crutching. After settling, the soap is pumped out of the kettle through the leg as shown in Fig. 303. The "crutcher" is a mixing-machine which derives its name from the early soap factories. This mixing was then done by hand with a wooden stick shaped like a crutch. The "crutcher" (Fig. 305) is surrounded by a jacket into which either steam for heating or water for cooling is introduced. It has an Archimedean screw for the stirring and in the center a cylinder over which the soap passes during the agitation. Any material such as sodium carbonate, sodium silicate, borax, starch, talc, grit or perfume can thus be incorporated into the soap. All laundry soaps carry some such filling, which is by no means an adulteration and

needs no apology for being present. The temperature at which the soap is dropped is carefully controlled in each crutcherful and regulated by introducing either steam or water to the jacket. Good results are obtained by keeping this heat about 140–144° F. When thoroughly mixed the soap, still semi-liquid, is dropped out of the bottom of the crutcher into frames. The pump is shut off when the nigre is reached and the nigre boiled up to be pumped out into a second rosin change.

Framing. These "*frames*" are tight boxes supported on a truck (Fig. 306) and hold one entire charge from the crutcher. The sides are bolted together in such a manner that they may be easily taken off when the soap is hard enough. This is called "*stripping.*" The time of "stripping" depends on the season—three days in winter and four days in summer. The soap should be stripped as soon as possible, as the soap cuts better when cool. With soap of good body, the cutting may be done the next day.

FIG. 308.—Power Cutting Machine.

Slabbing and Cutting. When the soap is hard enough, it is run through the "*slabber*" (Fig. 307). This is a machine with a cutting-head large enough to slab the whole frame at once. The cutting-head has wires drawn across it at spaces equal to the thickness of a cake of soap. Each slab is now put through the "*cutting-machine*" (Fig. 308) and given two cuts, one through its length and the other at right angles to it which turns out the slab completely cut into cakes. In the power cutting-machines of latest type the cut cakes fall, spaced, onto a rack which is lifted from the table and placed on a truck for transportation to the drying-room, which may be done artificially or allowed to stand in well ventilated rooms.

Pressing and Wrapping. The soap stands on these racks until the surface dries over enough so that it may be handled and pressed without marring it. This is called "*skinning over.*" Green or fresh soap acts very badly in the presses and is easily dented in passing to the wrapping-machines (Fig. 309), which run automatically and prepare the soap for the boxes.

Below are given two tables which show the general changes in composition which take place with each operation in the kettle on the soap and the resultant lyes.

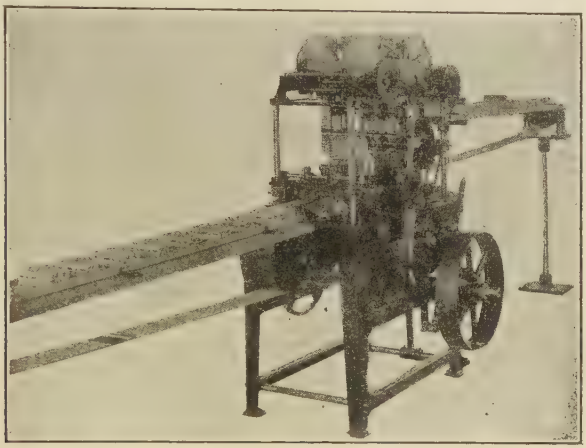

FIG. 309.—Wrapping Machine.

COMPOSITION OF SOAP DURING MANUFACTURE. (BOILED LAUNDRY SOAP)

	Glyc.	H_2O	Free.		NaCl.	Unsapon.
			NaOH	Na_2CO_3		
First change soap	1.66	36.87	Trace	.13	1.61	.49
Second change soap	.72	37.96	Trace	.11	1.43	.68
Third change soap	.48	39.38	Trace	.11	1.94	.50
Third change soap (over night)	.36	37.63	Trace	.11	1.82	.94
Fourth change soap	.23	35.91	Trace	.08	2.22	.68
First Rosin soap	.23	34.85	None	.08	3.59	2.41[1]
Second Rosin soap	.16	36.62	.30	.53	1.95	.96
Finish change (as steam was shut off)	.10	36.51	.01	.24	.70	1.07
Framing sample (after seven days)	.07	31.78	.01	.11	.30	1.15
Crutched soap		33.44[2]	.03	2.09	.32	
Pressed cake	.04	29.11[3]	.02	2.07	.33	1.38
Nigre	.42	55.86	.16	.58	1.71	.31

[1] Contains 1.30 per cent unsaponified rosin.
[2] Filling added.
[3] Tested four days after pressing.

LYES FROM THE ABOVE CHANGES

	Glyc.	NaOH.	Na_2CO_3.	NaCl.	Fatty Anhyd.	Comb. Alk.
First change	5.45	.19	.16	12.34	.19	.11
Second change	2.19	.16	.08	8.54	.13	.03
Third change	1.42	.07	.08	8.53	.06	.02
Fourth change	.68	.12	.09	11.17	.02	.01
First Rosin change	.53	2.63	.95	12.22	.21	.03
Second Rosin change	.53	2.88	.89	7.66	.25	.03
Third Rosin change	.43	2.32	.72	6.20	1.84	.26

The Twitchell Process. This process is a newer method employed in some soap factories for a treatment of the stock before soap-making, and has for its object a separation of the fat or oil into fatty acid and glycerine before it reaches the soap-kettle. It can be readily seen that the operation of making soap is then easier in the earlier or "killing" changes and removes the "salting-out" of soap in these earlier changes entirely as there is no glycerine to wash out.

Method. The fat or oil is first purified by steaming with about 1 per cent 60° H_2SO_4 for about two hours, after which the acid, impurities and water of condensation are drawn off. The melted and purified fat is run into a wooden tank, closely covered to exclude air. After heating up, 1 per cent of the "Twitchell Reagent" (sulfo-benzene stearic acid $C_6H_4HSO_3C_{17}H_{35}COO$) is added and the whole mass steamed for twenty-four hours with the addition from time to time of small amounts of H_2SO_4. After settling, the glycerine water (15 per cent glycerine) is drawn off and neutralized with lime and evaporated to a "crude glycerine" of 88–90 per cent glycerine content.

After the glycerine water is drawn off, the fatty acids are boiled with water and a small amount of lime, to remove all the soluble acids, air likewise being carefully excluded. After this neutralization is complete the fatty acids may then be stored in wooden tanks until ready for use.

The advantages of the "Twitchell process" are:

a A larger yield of glycerine
b. A purer and stronger crude glycerine.
c. A means of making rosin soaps in a crutcher without boiling the fat.

a. By changing the stock into fatty acid and glycerine before the actual soap-making is begun, an opportunity is afforded to entirely free the stock of its glycerine without the use of salt.

b. The crude glycerine obtained from soap lyes, called "*soap lye crude*," contains from 80 to 84 per cent of glycerol and from 7 to 10 per cent of salt. The crude obtained from the "Twitchell process," called "*saponification or candle crude*," carries from 88 to 90 per cent glycerol and only traces of salt. Salt is the worst part of the glycerine recovery where "soap lyes" are to be evaporated, as it keeps concentrating in the glycerine liquors during the boiling and requires the frequent dropping of these liquors during the process of making crude glycerine to eliminate this salt. Besides, the steam-chests of the evaporators become coated with salt during the boiling and insulates the heat.

The original "soap lye" solution contains about 3 per cent of glycerol while the "Twitchell" liquors carry about 15 per cent glycerol, thus saving a great deal of evaporation.

c. With the fatty acid at hand, it is possible to make soap directly

in the crutcher by the mixing of the fatty acid, alkali, saponified rosin and filling material.

The fact that the fatty acids produced are somewhat darker than the original stock has been the chief objection to this method of treating fats and oils. At present there are improvements being made in this process which claim to overcome this defect. If successful it will lead to a more general use among the soap-makers, as at present it is used chiefly by the candle-makers for producing stearic and oleic acids.

Soap or Washing Powders. These powders are mixtures of soda ash (dry Na_2CO_3), soap (mixed in liquid condition), and water, the only difference in the many kinds on the market being in the amount of these ingredients present and the kind of soap used. According to the amount of water present, there are two general classes: those containing 10 to 20 per cent of water being the old-style and those having 35 to 40 per cent of water, or the new-style, called usually "*fluffy powders.*"

Old-style Powder. As the soda ash comes in bags of 300 lbs. each, a mix or charge is based on a bag or multiple of a bag. The soda ash, soap (hot from the kettle) and hot water is dumped into a mixer and kept agitated until it begins to form in small lumps and then dropped to a table from which it is raked through a coarse screen, to allow as much heat as possible to escape and also to prevent the formation of big lumps. It is then shoveled on trays to cool and "set," the powder being kept below the height of the sides, and these trays tiered up to cool in a room provided with a good circulation. In this way, the process of crystallization (that of forming sal soda $NaCO_3.10H_2O$ in proportion to the amount of water used) will be complete in five hours under good conditions of humidity and ventilation. It can now be milled in mills of the Nell-Albright type. This mill has a round screen surface through which the powder is forced by a revolving arm or beater. The powder drops to a conveyer and is carried to the hoppers of the filling machines which automatically pack it.

Fluffed Powder. This powder is made in two ways, by the framing method or the continuous method.

Framing Method. The soda ash in the form of a strong (37-38° Bé.) sal soda solution is mixed with the soap from the kettle in a crutcher and dropped to a frame for the crystallization. When cool, the frames are stripped and the powder disintegrated.

Continuous Method. By this method the powder is mixed and cooled by means of a machine. This machine consists of two or three sets of hollow cylinders or rolls through which cold brine is circulating. These rolls being superimposed, the mixed charge is dropped on the upper set which forms in a thin layer on the surface and makes almost a revolution when it is scraped off on to the next set which are larger, and so on to the last set, by which time the crystallization of the Na_2CO_3 is complete and

the powder cooled. This powder likewise needs no milling but only a breaking up.

Discussion. The difference between the two general classes of soap or washing powders is in the amount of crystallized Na_2CO_3 present. The more water that is added to a powder, the more crystallized sodium carbonate will be formed and the smoother and softer the powder will be. In powders containing 10–20 per cent of water there is always some "heat of reaction" formed when water is added to it, owing to the rather large amount of uncrystallized Na_2CO_3 present.

The soap used is made in the usual way from cotton seed, corn, or linseed oils, cottonseed foots, distilled fatty acids and low grade greases and tallows.

ANALYSIS OF SEVEN SOAP POWDERS

	1	2	3	4	5	6	7
Moisture	13.39	23.50	14.07	14.53	34.32	37.79	40.35
Anhydrous soap	15.12	23.80	27.80	28.97	23.47	30.15	20.61
Sodium carbonate	71.55	51.81	57.90	56.18	41.87	31.93	39.09
Undetermined		.89	.23	.32	.34	.13	
Iodine value fatty acids	104.3	81.2	104.5	65.	85.8	84.8	99.2

Scouring Powder. This powder is made by mixing varying amounts of soap powder, silex (grit), talc and sometimes a small amount of sal ammoniac.

Scouring Soaps. These soaps are generally made on a cocoanut-oil base. The soap after saponification is drawn to a crutcher, silex (grit) is mixed with it and the mass dropped into an asbestos jacketed kettle or tank and run into slate molds to harden, each mold being the size and shape of the finished soap.

Boiled Toilet Soaps. The method of boiling for toilet soap is the same as for laundry soap, except that a different variety and grade of fat is employed. The raw materials consist mostly of vegetable oils to which a small amount of tallow is added. No rosin, however, is added as the vegetable oils possess sufficient lathering quality. On completion of the boiling operation the soap is run to a continuous drying chamber, where it falls on an endless belt and is slowly conveyed through the drying apparatus, coming out in the proper condition for the subsequent operations. An older method, and one which is still used in many factories, is to crutch, frame, slab, cut, and then "*chip*." The "*chipper*" (Fig. 310) consists of an enclosed disk provided with knives which revolve at a high rate of speed, and against which the bars of soap are pressed. The chips thus obtained are dried until brittle and are then ready for the subsequent operations.

Amalgamator. This machine (Fig. 311) is used for mixing the color and perfume with the chips before milling. With the use of an amalga-

mator a more uniform soap is obtained and at least one milling saved. In the old method of adding color and perfume to a soap, the chips were mixed in a box with color and perfume by a shovel. A uniform distribution of color and perfume was almost impossible by this method, and required five or six trips through the mill to produce the desired uniformity. An even mixture may be obtained in an amalgamator in about fifteen minutes, and twice milling this product is sufficient.

In the majority of toilet soap factories, in making up their stock they go in the order of their color, starting with white and then making the next darker shade, like yellow, then green, pink, etc., until they finish

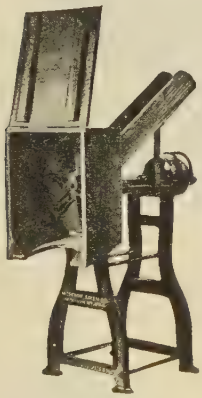

FIG. 310.—Chipper.

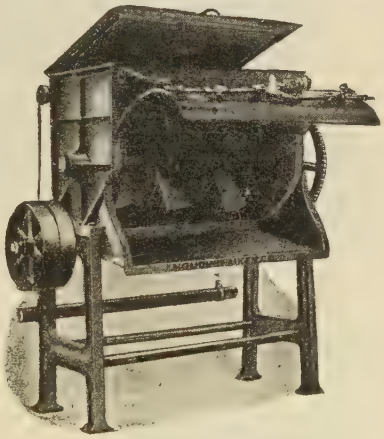

FIG. 311.—Amalgamator.

with the darkest soap, usually tar soap. In this way the machine will only need cleaning.

Milling. Whether the soap has been dried by the modern method or by the slower method of chipping it is placed in a mixing machine where the necessary perfume, color, or other ingredients are added. It is then fed to the "*mills*." These mills consist of two or more rollers (Fig. 312) between which the soap passes, thereby causing the added material to become well incorporated. The usual practice is to pass the soap between the rollers six times or until the corrugated flakes have a perfectly uniform and smooth appearance.

Plodding. The milled soap is placed in the hopper of a machine known as the "*plodder*" (Fig. 313), where it is subjected to great pressure by means of a compression screw. In the nozzle of the plodder is a "*forming plate*" having an opening the size of the cake desired. The flaky condition of the soap as it comes from the mills is converted into a continuous bar, which may be cut to any length and stamped or pressed as desired.

Milled soaps allow of the use of delicate perfumes or other materials

which would be destroyed if incorporated with the hot soap in the crutcher. The price of a soap depends largely upon the kind of perfume

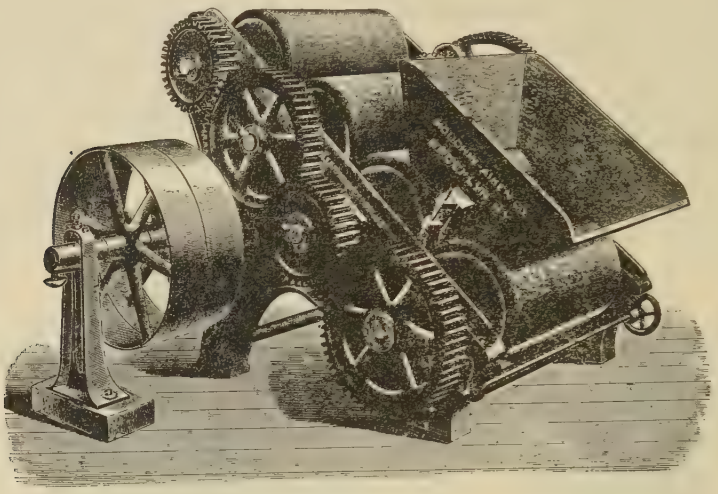

FIG. 312.—Soap Mill.

which is used to scent it, as out of the same kettle of soap may be prepared an article selling for ten cents or one dollar. Some toilet soaps are slightly superfatted so as to overcome the harsh effect of an alkaline condition.

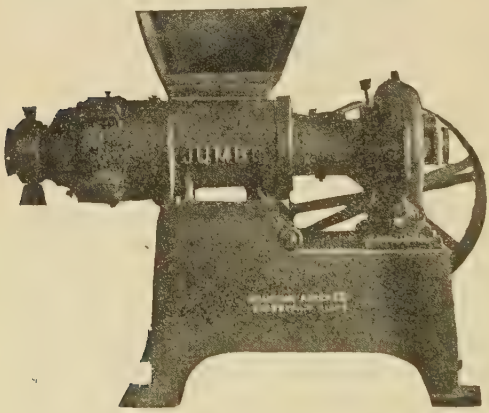

FIG. 313.—Plodder.

Soft Soaps. Soft soaps are usually prepared by employing potash as the alkali and an oil high in oleic acid as the fatty material. Saponified red oil, linseed oil, rosin, and cottonseed oil are among the chief oils used for the purpose.

Liquid Soaps. These soaps are made in the same manner as soft soaps and are given their liquid property by addition of glycerine or alcohol. Liquid soaps are made from selected stock and the lye well settled before using. Cocoanut oil is largely used for this variety of soap.

Half-boiled Soaps. As the name implies, soap made by this process is not boiled. The operation is always conducted in a crutcher, the

temperature of the stock being raised to about 160° F., and the lye added. The mixture of lye and fat is crutched for about five minutes and allowed to stand undisturbed for two hours. It is then crutched again until smooth, tested for excess of either fat or alkali, run into frames, allowed to set and harden as stated under boiled soaps. Half-boiled soaps contain all of the glycerine originally combined in the oil, and for this reason give a very satisfactory soap for toilet purposes. As there is no recovery of the glycerine it cannot be worked economically for laundry soaps. After settling and cooling, it may be chipped, milled, plodded, and pressed in the same manner as boiled soaps.

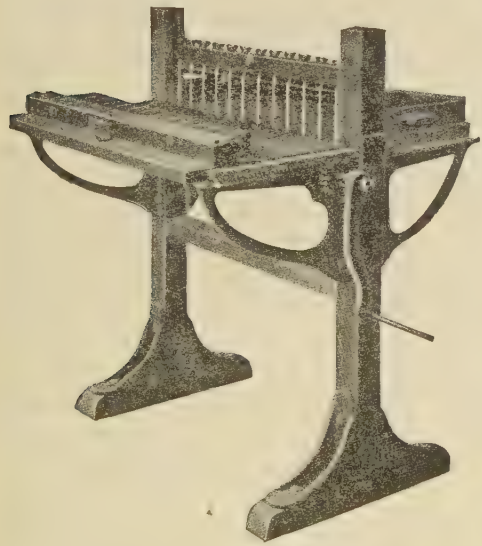

FIG. 314.—Toilet Bar Cutter.

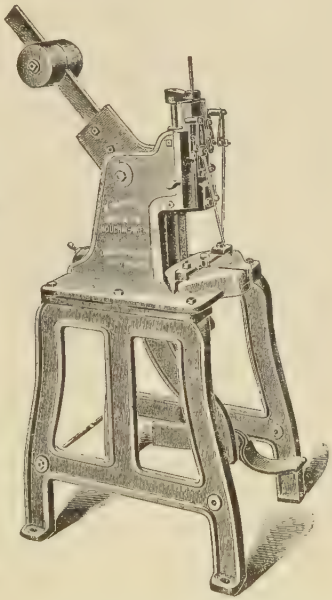

FIG. 315.—Toilet Soap Press.

Cold-process Soaps. Soap made by this process differs from half-boiled soaps in that the oils are only heated to their melting-point and the lye added. The operation is conducted in a crutcher and the mixture stirred until smooth, when it is dumped into the frames.

Floating Soaps. The soaps which float on water are prepared in the same manner as other soaps, and the specific gravity lowered by crutching at a high rate of speed, so as to pump the soap full of minute air bubbles. The same result is obtained by reversing the direction of the paddle several times during the crutching. Floating soap is never milled, but on cooling in the frames is cut into cakes and pressed.

Mottled Soaps. The old-style mottled soaps were made by boiling in a kettle over the open fire and run into frames to cool. During the long process of heating, certain decompositions took place, so that when

the soap cooled very slowly the excess of lye and impurities segregated to those portions which were the last to solidify. At present the same effect is produced by crutching with ferrous sulphate, ultramarine, lampblack, or other pigment just before the soap is run into the frame. Castile or Marseilles soaps sometimes have a green mottle, which changes to red on exposure. This is due to the presence of ferrous sulphate, which has been acted upon by the lye to produce ferrous hydroxide; which in its turn is changed to ferric hydroxide by exposure to the air.

Castile Soap. This soap is supposed to be made from olive oil and soda lye only, but as a pure olive oil soap becomes excessively hard and brittle on standing, other oils are usually added. The oils used for this purpose vary, cocoanut, linseed, cottonseed, and corn oil being usually employed. The color of the oil influences the color of the finished product, so that we have both white and green castile soap due to using either a light or colored oil. Practically all Castile soap is either made by the cold or half-boiled process.

Transparent Soaps. These soaps are usually made by dissolving a good soda soap in alcohol, decanting away from any insoluble matter and distilling off the excess of alcohol. This leaves the soap in the form of a transparent jelly, which is dried out in moulds having the form of the cake desired. Transparent soaps are also made by the cold or half-boiled process, by adding more glycerine together with a small amount of alcohol and any perfume or coloring matter which may be desired. A cheaper grade is made by adding a solution of cane sugar.

Shaving Soaps. These are usually soda and potash combination soaps, made from high-grade stock. They may be made on a cocoanut-oil base with the addition of stearic acid to give body, and a gum to keep the lather from drying. Many shaving soaps contain glycerine or sugar.

Shaving Creams. These are potash soaps usually made on a cocoanut-oil base to which is added a certain percentage of stearic acid.

Toilet Powders. Most toilet powders are composed largely of talc, to which varying amounts of calcium or other stearates have been added. Some powders also contain antiseptic substances such as boric acid.

Soap Powders for Toilet Use. These powders are prepared by completely drying a good grade of toilet soap and subsequently pulverizing it. They must be as near neutral as possible to avoid any irritation when used on tender skin.

Metallic Soaps. By adding soluble salts of the heavy metals to a neutral soap solution a precipitate of metallic soap is obtained. Some of these metallic soaps have very extensive application in the industries and in pharmacy. The lead soap produced by adding lead acetate to a linseed-oil soap is used as a drier in mixed paints. By boiling olive oil with lead oxide "lead plaster" is obtained.

CHAPTER XXIX

GLYCERINE

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Historical. Glycerine has only been known commercially some sixty years. It was discovered in the year 1779 by Scheele during his investigation of the action of litharge on fats, but years passed before the study and experience with the pure product showed the remarkable properties of glycerine, its permanence and non-volatility at ordinary temperatures, its softening effect on the skin and value in cosmetic preparations, its oily nature combined with its miscibility with water and alcohol, its enormous solvent powers, its sweet and agreeable taste, and finally its value as a base for the most useful of all explosives, nitroglycerine- and dynamite-properties, which are not met with in any other one substance, thus making glycerine an indispensable article.

About 1823 Chevreul published his researches on the constitution of fats, showing that instead of consisting of a single substance they were composed of fatty acids in combination with a base, glycerine, and that glycerine was contained in the waste liquors of the soap and candle factories. Processes for the purification of the crude glycerine were not available however until the early fifties, when pure glycerine was brought on the market by Sarg, of Vienna, and the Price Patent Candle Co., of London. Price's glycerine was a standard for many years. The demand for glycerine was enormously increased by Nobel's discovery of the value of nitroglycerine as an explosive in 1863. The only source of glycerine to-day is in the fats and oils occurring in animals and plants.

Constitution. Glycerine (sometimes termed glycerol) is a triatomic alcohol $C_3H_5(OH)_3$. The OH or hydroxyl group carries a hydrogen atom capable of replacement by acid radicles with the formation of an ester. Thus by the successive substitution of the hydrogen with the acid radicle of nitric acid there would be formed mono- di- and trinitro-glycerine with the formation of one, two and three molecules of water respectively. The fats are all triglycerides, all of the hydrogen atoms of the glycerol base being substituted by fatty acid radicles. Modern researches have

shown that these triglycerides are mixed in character, two or more different fatty acid radicles being combined with one glycerol group.

Sources of Glycerine. The world's output of crude glycerine is estimated at about 85,000 tons. It is exclusively a by-product industry of the soap and candle trades and the output depends not so much on the demand for glycerine as on the world's requirements of soap and candles. The cause of this condition is the relatively small percentage of glycerine obtainable from the fats, the theoretical amount ranging from 10.5 per cent with tallow to 13.5 per cent with cocoanut oil. In practice this is cut down by the free fatty acids always present, each 10 per cent of free fatty acids reducing the glycerine by about 10 per cent. With the increasing use of high grade fats for butter substitutes and the conversion of fatty oils to hard edible fats by the use of hydrogen and catalytic agents the soap- and candle-maker are compelled to resort to fats and oils of poorer quality than formerly. These fats are high in free acids and low in glycerine, so that the tendency seems to lie in the direction of lower yields in the future than in the past.

Glycerine is a by-product of the alcoholic fermentation of sugar, the amount produced being variously stated as 3–8 per cent of the alcohol formed. At any rate enormous quantities must go to waste in the residues from alcohol stills as to date no commercial process has been developed for the recovery of this glycerine.

Glycerine has been subject to wide fluctuations in price, the dynamite grade selling for 10 cents a pound in 1908 and 70 cents in 1917. The United States does not produce sufficient glycerine to meet its own requirements and there are from 30 to 40 million pounds of foreign crude imported annually in normal times.

Saponification. Only those industries requiring fatty acids in large amount can afford to produce crude glycerine. The candle-maker wants primarily the white, hard stearic acid. The soap-maker is after the combination of the fatty acids with soda in the form of soap and utilizes all of the higher fatty acids present. To separate the fatty acids from a fat it is necessary to break it up into its constituents. This process is called *saponification* and is brought about by the interaction of water and fat, fatty acid being split off and glycerine being produced. The decomposition with water alone is slow and requires very high temperatures. It is greatly facilitated by the addition of a catalytic agent, which may be of an acid or alkaline character. In the soap industry caustic soda is used, the soap formed emulsifying the fat and exposing a large surface of fat to the action of water. In the candle industry a small percentage of lime or magnesia is used, and the reaction hastened by a high temperature obtained by the use of autoclaves under a steam pressure of 250 pounds. In the Twitchell process, used by both the soap and candle industries, the catalyser is a sulfo-fatty acid, the hydrogen ion assisting the reaction and the sulfo-fatty acid acting as an emulsifier.

Another method on a different principle is the Connstein process depending on the action of an organic ferment derived from the castor-oil bean. According to the method of saponification used crude glycerines of widely varying properties are obtained. These are:

Soap-lye Crude Glycerine. This forms the principal source of supply. After the saponification of the fat by caustic soda the soap is thrown out of solution by the addition of salt. The mother liquor or spent lye containing 4–5 per cent glycerine, all the salt and the bulk of the impurities present in the fat, is purified by the addition of a crude persulphate of iron, obtained by the action of oil of vitriol on pyrites cinder or iron ore, or by the use of aluminium sulphate. A precipitate of the hydrate is thrown down carrying with it albuminoids and metallic soaps of the higher fatty acids. This is removed by a filter press. The purification is only a partial one and in case low grade stock has been used large amounts of impurities remain in the dilute glycerine.

The next step is evaporation, formerly considered a process of great difficulty when fire-heated kettles were used, as the salt caked on the sides of the vessel. The modern method is a concentration in a vacuum evaporator. At a vacuum of 27 to 28 inches the boiling point is reduced to such a point that the salt separating does not adhere to the heating tubes, but drops into a chamber placed below. Exhaust steam may be used during the greater part of the evaporation, live steam being used to finish off. The salt is raked out on a vacuum-filter and after washing may be used again. The crude glycerine when cold has a specific gravity of 1.30 or 33.5° Bé. It is a saturated solution of mineral salts in glycerine and water. The salts consist largely of sodium chloride with some sulphate and the sodium salts of the lower fatty acids. It is slightly alkaline with soda. The glycerine is usually about 80 per cent. It may run down to 60 per cent in bad crudes and up to 88 per cent in highly concentrated crudes of the best quality. The organic matter not glycerine will average 2–3 per cent in good glycerines. The ash will run from 8–10 per cent in good crudes; 15 per cent and more in bad crudes and crudes carrying solid salt.

Soap-lye crude may be easily recognized by its high salt contents when tested by silver nitrate, giving a heavy curdy precipitate. With basic lead acetate a heavy precipitate of oxychloride of lead is obtained. The specific gravity is high.

Saponification Crude Glycerine. This is the by-product of the candle industry and the glycerine obtained when fats are split up by the Twitchell process, the fatty acids being used in the candle or soap trades. It is free from sodium chloride and practically free from mineral matter in the purer grades. The thin liquor from the autoclaves or Twitchell saponifying tanks after settling to separate the free fatty acids is treated with a little lime or aluminium sulphate and filter-pressed. It is then evaporated to a specific gravity of 1.24 at 60° F. or 28° Bé. The gly-

cerine standard for saponification crudes is 88 per cent. In poor grades it will sometimes run down to 82 per cent and less and occasionally is as high as 90 per cent in high-grade crudes. The ash standard is 0.5 per cent and the organic residue 1 per cent although these figures are sometimes greatly exceeded. As a rule Twitchell saponifications are inferior to the autoclave crudes, not because the process is at fault, but because the Twitchell method makes available the use of low-grade fats and greases, which cannot be profitably treated in the autoclave.

A saponification crude is distinguished from a soap-lye crude by the absence of salt as shown by the silver nitrate test, by its low specific gravity and small precipitate with basic lead acetate. The latter may be heavy in bad crudes but is of a flocculent character and easily distinguishable from the precipitate of lead oxychloride. Basic lead acetate affords a good method of finding the quality of saponification crudes as a high-grade product gives only a slight precipitate.

Crude glycerines produced by the fermentation process are but rarely met with.

Purification. Crude glycerine contains mineral impurities such as salt, sodium sulphate, carbonate, hydrate, acetate, butyrate, caproate, etc., together with iron, lime, arsenic, and other metals. As volatile impurities may be enumerated fatty acids split off from the sodium salts, acrolein produced during distillation, ammonia and amines, sulphur compounds and trimethylene glycol. The last-named is contained in low-grade crudes derived from products subject to fermentation. There are also non-volatile organic substances present, such as albuminoids, resinous bodies and polyglycerols.

The only method used for the separation of glycerine from these substances is distillation combined with fractional condensation. By careful distillation the non-volatile substances are left behind in the still, and by careful control of the temperatures of the condensers the glycerine is condensed before the more volatile impurities.

Pure glycerine boils at 290° C. Saponification crude has a higher boiling point and soap-lye crude a still higher one because of the impurities in solution. At 290° C. there is considerable decomposition of the glycerine with formation of acrolein and polyglycerols, particularly in presence of impurities, and it was soon found that the glycerine could be distilled at lower temperatures and with less decomposition when the heavy vapors were carried over by steam. In the eighties vacuum distillation was first used as it was discovered that the boiling point of glycerine was materially reduced and the distillation facilitated by the use of a vacuum in the stills and condensers. This was combined with a steam jet, the steam being condensed to water before the vapors reached the vacuum pump. The source of heat was either a fire under the still, which also served as a superheater for the steam coil, or a closed coil

in the still connected with a high-pressure boiler and a separate superheater for the steam jet. The condensers were a series of air-cooled drums or pipes followed by water-cooled receivers, the glycerine being condensed in the hot air-cooled drums and the steam carrying some glycerine and volatile impurities in the water-cooled receivers.

The various steps will be made clear in the following descriptions showing the historical development of the processes. The illustrations and part of the text are taken from articles by Wood and Langmuir, published in the "Transactions of the American Institute of Chemical Engineers," Vol. 2, 1909.

It is not improbable that the first form of apparatus used for distilling glycerine was on the principle of that shown in Fig. 316, which is a direct-

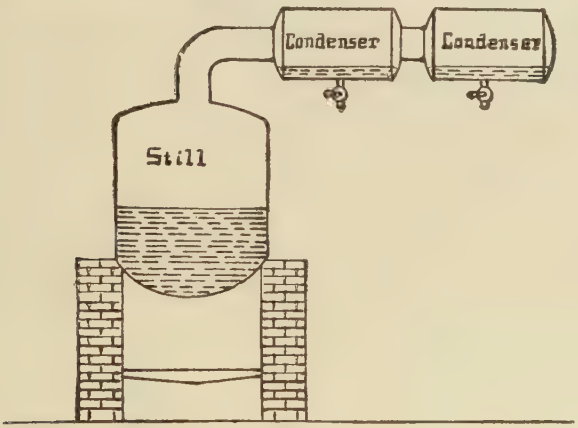

Fig. 316.

flame-heated still connected by piping to a condenser. The manufacturing cost of distilling glycerine with this simple apparatus would be too great to permit of its use at the present time. This cost would be due to waste of glycerine by decomposition. The glycerine would vaporize at the temperature of the boiling point of glycerine in air. The fuel used per pound of glycerine distilled would be much less than is used in modern practice. It is very much more economical to vaporize the glycerine at a lower temperature and to use more fuel, but decompose less glycerine.

Steam Distillation. One of the earliest types of apparatus used to lower the distilling temperature of glycerine is that shown in Fig. 317. The jet of steam issuing from the nozzle in the body of glycerine near the bottom of the still causes the glycerine to vaporize below the boiling temperature, but, after the combined steam and glycerine vapors pass through the air-cooled condensers where most of the glycerine will be condensed, it is impossible to prevent some glycerine from passing out into the air along with the steam. Glycerine will not all condense out of steam after the two vapors have once mingled together, so that

the only way to recover all the glycerine that has left the still as vapor is to provide means to condense both steam and glycerine, and afterwards evaporate the water out of the glycerine. Fig. 318 shows this next step in advance, which is a cold-water condenser added in series with

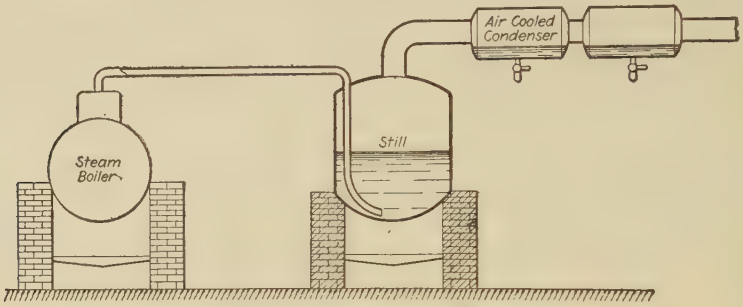

Fig. 317.

the air-cooled condensers, and an evaporator to evaporate the water that is condensed along with the glycerine in the cold-water condenser.

When glycerine distillation was in this stage of development, a superheater, as shown in Fig. 318, was added for superheating the steam flow before entering the still. It is remarkable that up to and including

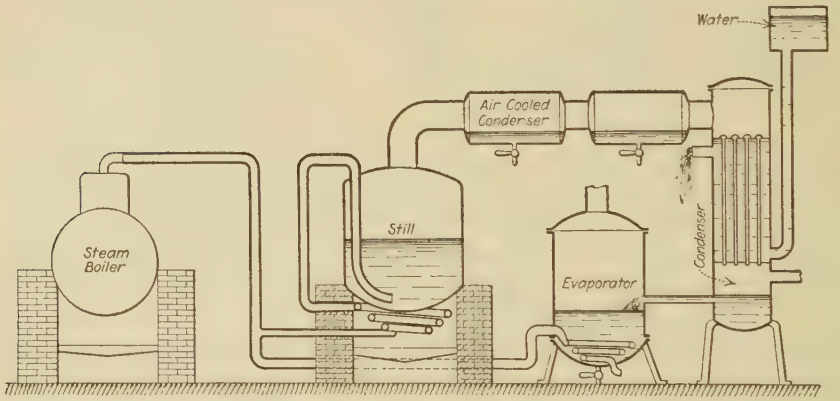

Fig. 318.

this economy in manufacturing, the fuel used per pound of glycerine distilled became greater at each step.

Vacuum Distillation. There was still further room for improvement in preventing decomposition by reducing the vaporizing temperature. The vacuum pump shown in Fig. 319 was the means of reducing this temperature. Also, considerable steam was saved by evaporating the "sweet-water" in evaporators arranged as double effects, which will be

also seen in this figure. There are some glycerine distilling plants of the type shown in Fig. 319 operating to-day.

Jobbins and Van Ruymbeke Process. In the Jobbins and Van Ruymbeke apparatus, shown in Fig. 303, the principal and almost the whole difference between it and the earlier type shown in Fig. 320 is in abolishing the direct-fire heat under the still and substituting therefor steam-heated coils, both for superheating the flow of steam and for

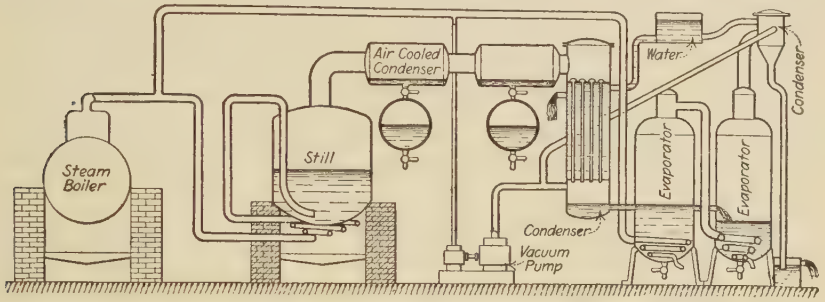

Fig. 319.

heating the body of glycerine to be vaporized. Fuel can be saved by heating the glycerine by this method, as the bottom of the still will not compare in value with the heating surfaces of a steam boiler in absorbing heat from a fire—more heat will pass up the chimney from the furnace of the still than from the furnace of the boiler.

Heckmann System. In the Heckmann apparatus shown in Fig. 321, the next advance was made in the saving of fuel, as in this apparatus

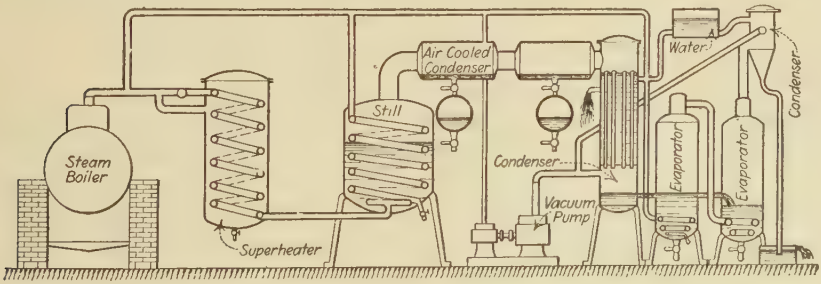

Fig. 320.

there is possibly but little " sweet-water " to be evaporated. There are no air-cooled condensers in this type. The glycerine condenser is made up of a vertical series of annular pans fitting tightly in a cylindrical shell. Over the hole in the center of the pan, but sufficiently out of contact to freely permit a passage for the flow of vapor, are inverted dish-like covers—the edge of the covers being below the level of the edges of the pans.

The level of the liquid in the pans is maintained just above the edges of the covers by means of overflow pipes adapted to permit a flow of liquid from the higher to the lower pans whenever the liquid reaches the overflow level. Above the glycerine condenser is a small sweet-water condenser adapted to condense a small portion of the vapor that passes through the glycerine condenser. The whole arrangement is such that the steam and glycerine vapors coming from the still must bubble up through the liquid contained in the pans, which is a mixture of water and glycerine; the water evaporates and the glycerine condenses.

The small sweet-water condenser at the top supplies the water to the pans, which in quantity should not be very far from the quantity of glycerine condensed in the condenser. The vapor which is not condensed in the sweet-water condenser is finally condensed in an ordinary condenser,

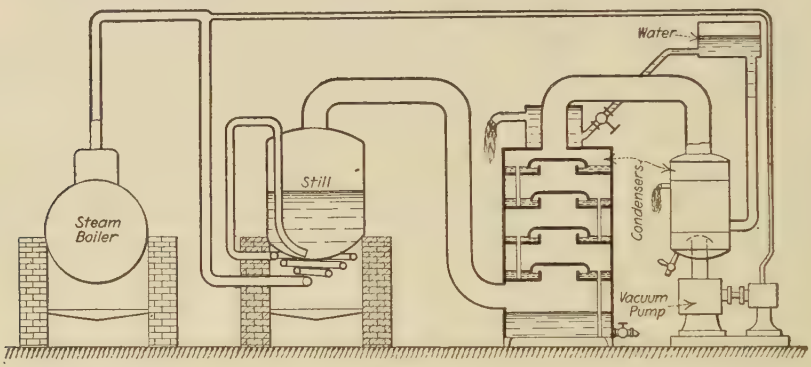

Fig. 321.

and according to the claims of the inventor contains so little glycerine that it can be run to the sewer.

Garrigue System. In the Garrigue system, Fig. 322, an economical superheating of the steam, as well as the condensation of some of the glycerine, are both obtained in the same piece of apparatus. The heat supply of this superheater is furnished by the hot vapor coming from the still which flows around the tubes of the superheater, while through the tubes passes the steam supply of the still. This steam supply is the vapor arising from the "sweet-water" as it evaporates in the evaporator. This is one of the features conducive to the fuel economy of this system.

What glycerine is not condensed in the superheater is mostly condensed in a surface condenser, through the tubes of which circulates warm water. In all the above-described systems evaporating—if any is done—is accomplished by steam directly from the boiler, or exhaust from the engine.

Wood Process. In the Wood multiple-effect apparatus, Fig. 323, economy of fuel is obtained by using but one flow of steam to a number of

stills and condensers, the stills being arranged in series in regard to the steam flow; that is, the steam from the steam jet of the first still flows through a series of stills alternating with condensers, the condensers being maintained at a temperature that will condense glycerine out of the steam but not the steam itself. The glycerine that is vaporized in each one of the series of stills flows along with the steam to the condenser next in line, the glycerine being condensed while the steam passes on to the next still.

The rather high condensing temperature in the condensers is maintained by using water boiling under a low pressure as a cooling agent. The steam generated from this boiling water of the glycerine condensers is used to evaporate " sweet-water " and also to evaporate the water from which the steam flow of the stills is derived. This steam flow is generated in an evaporator which is fed with distilled water, so that no impurities will be carried over to the stills, with the steam. The heat absorbed in

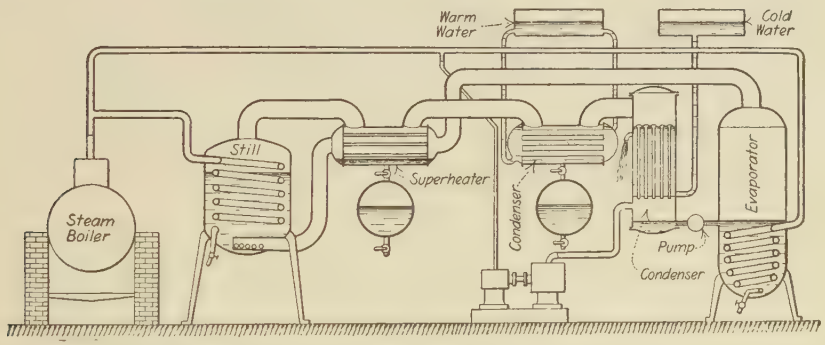

FIG. 322.

the vaporization of the glycerine is recovered when it is condensed in the boiling-water condensers. The heat thus transferred is sufficient to supply all the steam necessary for the stills and a large proportion of that required by the sweet-water evaporators. There is no difficulty in utilizing the exhaust steam from the engines, as there is always considerably more " sweet-water " to be evaporated than that which is condensed in the cold-water condenser or last condenser of the series. Washings from filter-presses, etc., are a source of much sweet-water.

An arrangement of stills and condensers in series along a single flow of steam necessitates a free flow without obstructions. Passing the steam flow from one still to the other of a series, and mingling it with the glycerine by steam jets beneath the surface, is out of the question in this system, as too much back pressure would result from overcoming the hydrostatic pressure of the body of glycerine in each still. The first stills of such a series would be working at a great disadvantage, due to a low vacuum. The lower the vacuum the higher must be the distilling

temperature to get a good output, but a high distilling temperature is a cause of decomposition. In this system, instead of forcing the steam down through the body of glycerine, the glycerine is pumped up and sprayed down through the steam, and no back pressure to the flow of steam results.

The steam economy of this system can be better appreciated by referring to Fig. 323, and following the course of the heat flow from the boiler to the final cold-water condensers. It will be seen that it leaves the boiler through the steam main, is carried along in the steam principally as latent heat. A portion is taken to operate the engine and vacuum

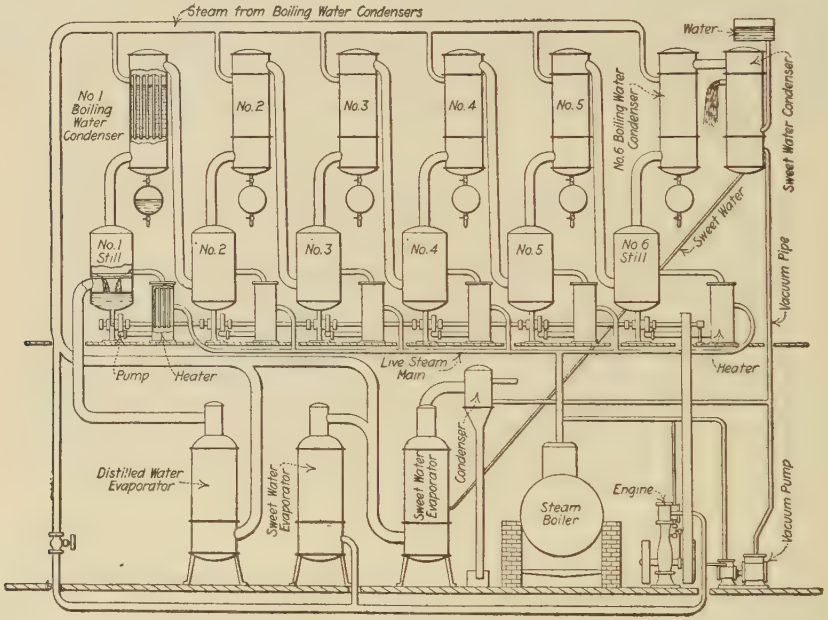

Fig. 323.

pump, but the larger flow divides and passes to the heaters of the six stills. The heat is here taken up by the glycerine, passes, in the process of vaporization, to the steam and glycerine vapor, and is carried to the glycerine condensers, where it is transferred to the steam arising from the boiling water therein.

The six flows from the boiling-water condensers then come together into one. On the way to the evaporators the flow again divides, the larger portion going to the distilled-water evaporator and the smaller portion joining forces with the flow of heat from the first effect of the sweet-water evaporators, which receives the heat of the exhaust of the engines, passes to the second effect of the sweet-water evaporators, then along with the vapor to the jet condenser.

Going back to the flow of heat to the distilled-water evaporator, the heat flow passes into the pure steam arising from this evaporator, then is carried again to the stills; but this time, instead of dividing into a flow for each still, there is but a single flow passing from one to the other through all the stills and condensers and finally to the cold water of the sweet-water condenser.

It will be noted that in this process the glycerine instead of being heated by direct fire under the still, or by closed steam coils in the still, is taken from the bottom of the still by a centrifugal pump and forced upwards through a heater containing a number of small tubes surrounded by high-pressure steam.

The heating surface of the heater, and therefore the speed of distillation, can be increased to a point which cannot be reached by closed coils in a still. The rate of flow of the glycerine through the heater is dependent on the speed of the centrifugal pump and may be adjusted to the best conditions. The steam-pressure maintained in the heater determines the temperature of the heating surfaces. As the three conditions mentioned are variable within wide limits any desired distilling temperature may be obtained and held within narrow limits. There is no difficulty with the tubes of the heater becoming clogged with salt or organic deposits, for the current prevents any deposition of solid matter. Only enough glycerine need be taken to fill the connections and heater. Under the old process a considerable body of glycerine must be kept in the still to obtain the full heating effect from the coils, which extend nearly the entire height of the still, and to prolong the contact of glycerine and steam from the open jets, so as to enable the steam to take up its full charge of glycerine vapor. A large excess of glycerine over and above that distilled must therefore be kept in the still and maintained at a high temperature for a long time.

In this connection the patent of Classen (German patent 198,768, 1907) is interesting. Classen obtains diglycerol and polyglycerol by heating anhydrous glycerine with small quantities of alkali or alkaline soaps. Prolonged heating of crude glycerine containing such impurities in the average still must result in loss.

In the Wood process the glycerine is hot and anhydrous and there is no interruption of the distillation on account of stops for filling up or blowing out. A set of six stills in series, using one steam supply, is now successfully in use with no diminution in efficiency of the last still as compared with the first. All the stills in a series are under the same vacuum, which is uniform, as there is no necessity for breaking the vacuum, as must be frequently done in the old system whenever the stills are emptied and charged. It is noteworthy that in this system the hot glycerine superheats the steam.

Products. Whatever the process of distillation the distillate will consist of a heavy portion, usually almost anhydrous glycerine, condensing

in the hot condensers and a "sweet-water" consisting of the condensed steam used in the distillation, together with the volatile impurities and a little glycerine. The "sweet-water" is evaporated to recover the glycerine and must be redistilled.

Dynamite Glycerine. The heavy portion of the distillate may be taken for dynamite grade after bringing it up to a gravity of 1.262 at 60° F., by heating under a vacuum in an evaporator. Dynamite glycerine is sold on a basis of specific gravity and freedom from impurities, especially salt. The gravity is ascertained by the pyknometer, and must be at least

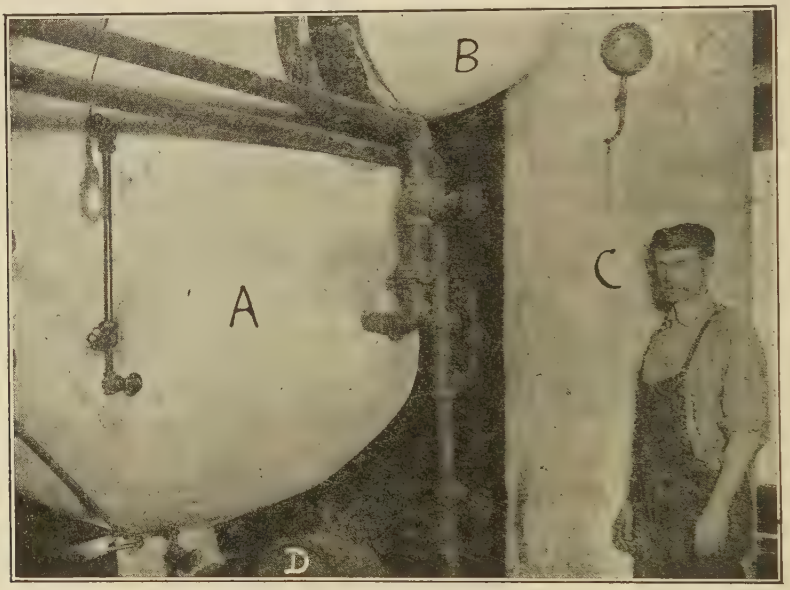

FIG. 324.—Wood Multiple-effect Stills.
A, Still; *B*, Steam inlet; *C*, Heater; *D*, Circulating pump.

1.262 at 60° F., referred to water at the same temperature. Chlorine must not exceed 0.01 per cent. Ash must not exceed 0.10 per cent.

Chemically Pure Glycerine. With good grades of crude and careful handling selected portions of the distillate are sometimes taken for the chemically pure grade.

As a rule, however, chemically pure glycerine is prepared by a second distillation with steam in vacuo and the final product is treated with cyanide black and filter-pressed to remove the slight color and clarify the glycerine. Chemically pure glycerine as required by the United States Pharmacopœia need only be of 95 per cent strength, which corresponds to a specific gravity at 60° F. of 1.252. It is commonly prepared by the addition of the necessary amount of distilled water to the glycerine obtained in the hot condensers. The strength may be found more accu-

rately by specific gravity than by analysis, provided a correct table is used. Of those published the Gerlach is the most accurate. Standards of purity are defined in the U. S. Pharmacopœia, 9th Revision, 1916.

Foots. The residue of organic matter and salts which accumulates in the still toward the end of the distillation is called foots. In some plants the distillation with steam is continued until portions of the condensed distillate show the specific gravity of water, when it is assumed that all of the glycerine has been extracted and the residue is boiled up with water and blown out to the sewer. In other cases the crude glycerine is distilled down until the foots carry 40–50 per cent of glycerine and are still fluid when hot. The residue is blown out of the still, thinned down with "sweet-water," press-washings, etc., and treated with aluminium sulphate or persulphate of iron to precipitate organic matter and filter-pressed. The filtrate is concentrated and the resulting crude either distilled for itself or mixed with fresh crude.

Another method of foots treatment is acidification with sulphuric acid after dilution with "sweet-water." A scum of black, tarry matter is skimmed off and the liquid filtered through bags. The acid filtrate is concentrated in a cast-iron evaporator and a considerable part of the free fatty acids present are eliminated with the steam.

Yield. There are but few published statements as to glycerine loss in refining. The factory should be charged with the amount of anhydrous glycerine as found by analysis in the weighed crude delivered to the works. The distilled glycerine produced is multiplied by the percentage of glycerine as ascertained by specific gravity tests, usually 99 per cent with dynamite glycerine and 95 or over with chemically pure. The difference between the receipts and outgo, divided by the amount of crude worked, multiplied by 100, is the percent loss.

Lewkowitsch states that losses incurred by faulty methods are large, and range from as much as 15 to even 40 per cent. In an editorial in the Jour. Industrial and Engineering Chem., 1911, 4, the statement is made that "good soap-factory practice will recover from 80-90 per cent of the glycerine in the fats saponified, and of this the still will win 97 per cent or more. These are good yields and the percentage in many factories will not run so high." Hinckley gives the loss as 5 per cent and Davis as 4 per cent. (See literature.)

Glycerine is shipped in plain or galvanized-iron drums of 55- or 110-gallon capacity, corresponding to 550 and 1100 pounds respectively, and in 50-pound boxed tin cans.

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Very complete articles on the technology of glycerine from the German standpoint may be found in Ubbelohde " Handbuch der Chemie und Technologie der Oele und Fette," Vol. 3, 1–126, Leipzig, 1910. See also Lach, " Die Gewinnung und Verarbeitung des Glycerins," Halle, 1907, 88 pages.

The American methods are very fully described up to 1906 by Lamborn, in his book, " Modern Soaps, Candles and Glycerine," New York, 1906. See also Hinckley, " Recovery of Glycerine from Spent Lyes," Jour. Society Chem. Industry, 1907, 26, 596. Garrigue's process is described by Moore, Jour. Industrial and Engineering Chem., 1910, 282–293. The Wood process is discussed in the " Transactions of the American Institute of Chemical Engineers for 1909. Questions of analysis are fully treated in the Reports of the Glycerine Sub-committee of the American Chemical Society, and published in the Jour. Industrial and Engineering Chem., 1909, 44, 268; 1910, 222–229; 1911. 679–686. Further reports will be issued from time to time.

Specific gravity methods are described by Comey and Backus, Jour. Industrial and Engineering Chemistry, 1910, 11–16.

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CHAPTER XXX

LAUNDERING

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Growth of the Industry. The growth of the power laundering industry during the thirty-five or forty years since its initiation in this country has been almost phenomenal. Laundries were included in the 1910 report of the Census Bureau for the first time. The number of power laundries given is 5184 which does not include hotel, factory or institutional plants. From these figures it will be seen that power laundering has a much greater commercial importance than is generally supposed.

Among the numerous factors which have made this rapid development possible, the two following may be cited as the most important. First, the marked changes which have occurred in the social and economic conditions throughout the country, and second, the great advances made in laundry practice as a result of the ingenuity displayed by progressive launderers and manufacturers of laundry machinery and supplies.

Most satisfactory results have been obtained in the invention of new kinds of labor saving devices, and it must be conceded that the standard of excellence of the mechanical equipment in the laundries compares favorably with that of other kinds of machinery. Relatively more remains to be done in bringing the chemical side to an equally satisfactory level. Only recently has the value of introducing methods devised in accordance with a knowledge of chemical principles been realized, and in a majority of plants "rule of thumb" methods are still followed.

Nothwithstanding this fact, and in spite of it, the quality of work which can be obtained by the use of machinery and supplies now available and in use is very good. In fact, many laundries do a grade of work that is excellent in appearance and do it with comparatively little injury to the fabrics. It is the small, poorly equipped, and badly managed laundries which are responsible for the prevalence of the notion that the steam laundry at its best is a failure. Although the possibilities in this field have by no means all been realized, much has been accomplished and the future certainly holds much in store.

The practice of doing laundry work in the homes and by the help of washerwomen has become less general, as the quality of the work done by the power laundries has improved. It seems inevitable that the change shall continue at an increasing rate, for the laundries will be enabled to do better and cheaper work, and to observe better sanitary conditions as improvements continue to be introduced.

The laundering industry is not to be classed as a purely chemical industry, but like many others which are largely mechanical, its successful operation depends on the proper combination of mechanical and chemical processes. Besides those chemical reactions which are essential parts of the work, there are others which occur, under certain conditions, as objectionable irregularities. The more extensively the details of both of these classes have been taken into consideration and controlled in a given plant, the more uniform and satisfactory have been the results obtained. For these reasons a brief description of the methods employed in a modern power laundry may not be without interest and value to chemists.

The launderer's business is the cleansing and subsequent finishing for use of textile fabrics, and this is necessarily custom work. For this reason, the methods employed will be different in different localities, but the essential features are quite similar throughout the country. The laundering problem is a complex one, on account of the great variety of fabrics to be handled, and the large number of dyestuffs now used complicates the matter still further. On account of the differences in the chemical properties of the various fibers and dyestuffs, numerous methods of treatment are necessary for the different classes of articles. Those textile fibers most largely used are cotton, flax, wool, and silk, woven either separately or in different combinations. The list of dyestuffs is an extremely large one. For the successful performing of laundry work, a knowledge of the chemical properties of these different fibers and dyes is essential.

Another factor which causes differences in the processes employed is the nature of the substances to be removed and the extent to which the articles are soiled. It is difficult to classify these substances, but roughly, divisions may be made as follows: Albuminous substances, such as blood and egg stains; vegetable dyes which cause fruit and wine stains; fats and oils, including hydrocarbon greases and oils; acid and alkali stains; body excretions and waste epithelial cells; old starch; street dirt and soot.

For convenience of treatment, the work of the laundry may be divided into several parts. These include generation of power, collection, listing, marking and sorting of the articles, washing, starching, drying, dampening and ironing, followed by finishing and preparation for distribution. It is obvious that many of these operations are not based on chemical principles, and these will be described only briefly, in order that the connection between the various steps may be apparent.

Marking. After collection, the bundles are brought to the marking room. There they are opened, all articles not already marked are marked with an indelible ink, and a list of each customer's articles is made. Machines operating on the typewriter principle, allow the marking to be done neatly and quickly, and a tabulator, recently invented, makes and prints a correct list of all the articles. The sorting into lots of the same kind is next done, when the articles are ready for the washroom.

Washing Machine.[1] This part of the process is the one which employs chemical reactions more largely than any of the others. The proper handling of the articles in the washroom is absolutely necessary for the turning out of properly finished work, and also for the prevention of excessively harmful action to the fibers.

Fig. 325.—Washing Machine.

The machines, Fig. 325, in which the washing is done consist of two concentric wood cylinders (the inner one is often brass) with a space of several inches between them. The outer cylinder is stationary and is connected to the water and steam pipes, and also to the drain pipe. The inner cylinder, into which the clothes are placed through a hinged door, is perforated with a series of small holes, which allows the liquids introduced to partly fill both cylinders. For the purpose of forcing the solution through the fabrics, the inner cylinder is revolved, and an automatic reversing device operates at regular short intervals. All of the solutions with which the articles are treated are introduced into the washer in succession, and the clothes are not removed until they are finished and ready for the extractors, which are centrifugal drying machines.

Detergents. The detergents used are water, soap, carbonate and bicarbonate of sodium and potassium, sodium hydroxide, borax, and

[1] The illustrations in this chapter are from the American Laundry Machinery Manufacturing Co., Chicago, Ill.

mixtures of carbonates and bicarbonates, sold under trade names as washing sodas. In choosing a substance from the list, not only should its action as a cleansing agent be considered, but the possibility of its attacking the fabrics should not be lost sight of. Soaps are unquestionably the best detergents, and the practice of adding large quantities of alkaline substances to them is not a good one, in case a soft water is being used. Neutral soaps, to the solutions of which small quantities of soda ash may be added, are preferable to strongly alkaline soaps, which are generally used in ignorance of their alkaline content. Experiments have shown that soda ash is just as satisfactory as the prepared washing sodas provided it be used properly, and it has the advantage of costing less. Prejudice against the use of soda ash seems to be due to the fact that it is used in too large quantities, since the amount of washing soda called for in the regular formula is simply replaced by a like quantity of soda ash, when a change is made. Since the washing sodas are approximately half soda ash and half sodium bicarbonate (exclusive of the water content) it is seen that a much smaller quantity of soda ash should be taken to give an equally strong alkaline solution. Alkalies react readily with wool and silk, but do not attack cellulose appreciably unless the solutions are concentrated. The chief objection to their use with cellulose is the production of a yellow color, even if the solutions be relatively weak.

Laundry Soaps. The best soaps for general use are those made from good grades of red oil—crude oleic acid. They are much more soluble than tallow soaps, and the oleates have, in addition, more pronounced detergent action than the palmitates and stearates. This greater solubility is an advantage, since it permits more efficient removal of the soap by rinsing. Resin soaps are inferior as cleansers, and furthermore they produce a yellow cast in the fabrics when used repeatedly.[1]

Theory of Washing. For many years the detergent action of soap has been a subject of much interest to chemists, and consequently a large number of theories has been advanced for its explanation. It is interesting to note that all of these theories, except one,[2] start from the same premise, as regards the condition of the substances to be removed, the dirt. According to this assumption, all dirt adheres to fabrics because of a film of fatty substances, and only when the latter is removed is it possible for the dirt particles to be loosened and carried away by the suds. The point of difference between all of these theories, with the one exception, is simply the manner in which this film is thought to be destroyed. Although this cause for the adhering of dirt particles is undoubtedly operative in many cases, it seems very

[1] H. L. Jackson, Cantor Lectures, 1907; also Dafert and Wolfbauer, *Oester. Chem. Ztg.*, 1908, No. 12, abstracted in *Chem. Abstracts*, 1909, p. 1224.

[2] W. Spring, *Zs. für Chem. und Ind. der Kolloide*, IV, 161 (1909), also *Rec. Trav. Chim. des Pays-Bas*, XXVIII (2 série, XIII), p. 120.

likely that the conclusion that it is exclusively true is unwarranted—it at least lacks experimental proof. Whatever may be thought of Spring's theory, it must be admitted that his experiments show that soap possesses marked detergent properties under conditions where a fatty film is certainly absent. No one of these theories seems to account for all of the known facts, and the problem still lacks an entirely satisfactory solution.

The earliest theory is that of Chevreul, which was published in the report of his researches on animal fats (1811–23).[1] These investigations showed that soap is decomposed into free alkali and acid salts of the fatty acids when it is dissolved in large quantities of water. The alkali thus formed is assumed to be most largely responsible for the detergent properties, which are accounted for as follows: By a simple saponification of the fats by this alkali, the dirt particles are thought to be left free and carried away and prevented from settling in the fabrics by the acid salts of the fatty acids, which constitute the suds. This explanation is an ingenious one, and has for many years been most favorably received. However, there seem to be objections to it which are insurmountable.

It is true that soaps do undergo hydrolysis, but with soap solutions of the strength ordinarily used—only several per cent of soap—the quantity of alkali produced by the reaction is necessarily small, since measurements of the per cent of hydrolysis give small values.[2] Since saponification at best is one of the slower chemical processes, it is inconceivable that this weak alkaline solution could exert an appreciable action on the fats in the short time necessary for washing. Besides, solutions of the alkalies of the same, or even greater strength, are inferior as cleansers.

A theory which seems to be supported by a larger number of facts assumes that the detergent properties must be ascribed to the emulsification of the fats which are the cause of adherent dirt.[3] The properties which seem to be most closely connected with the detergent action are a high surface viscosity and a low surface tension, both of which are possessed by soap solutions to a marked degree.

Besides the breaking up of the fatty film the power of wetting oily surfaces and of lubricating dirt particles and fibers must be considered important factors in the cleansing process. Hillyer has shown by a number of experiments that these properties also are due to the undecomposed portion of the soap and not to the alkali formed by hydrolysis. A method for grading commercial soaps which is based on this theory,

[1] Chevreul, "Recherches chimiques sur les corps gras d'origine animale."

[2] H. L. Jackson, Cantor Lectures, 1907.

[3] Hillyer, *J. Am. Chem. Soc.*, XXV, 511-32, also 1256-65. Also Donnan, *Ibid*, XXV, 1215 and Z. physik. Chem., **31**, 42.

has been devised by Hillyer. The surface tension of solutions of the different soaps against a standard hydrocarbon oil is measured by the drop method. The values obtained classify the soaps in the order of their usefulness as detergents, since solutions having low surface tensions are shown experimentally to be superior detergents.

As an amplification of the above theory another has been advanced which includes the influence of pedesis, or the so-called Brownian movement, in affecting the size of the dirt particles.[1] Experiments are cited which are interpreted as proving that the bombardment of attached dirt by the microscopic particles in suspension which show the Brownian movement causes a disintegration of the dirt into portions small enough themselves to exhibit pedesis. W. S. Jevons[2] had published a theory which is quite similar to the above, but which did not ascribe as large a part to the emulsification of the fats.

The peculiarity about Spring's theory[3] is that he proposes a new reason for the adherence of dirt particles to fibers, namely, the formation of a dirt-fiber adsorption compound. The explanation of the cleansing action of soap solutions is given by the formation of more stable soap-dirt adsorption compounds, which are carried away by the mechanical action exerted during the washing process. This removes the problem to the field of colloid chemistry, a branch of the science which is just now experiencing a wonderful growth. Although many facts are enumerated in support of this theory, it would seem that it has not assumed its final form, as yet.

Classes of Fabrics. The nature of the treatment is conditioned by the kind of fabrics being washed, and a number of classes might be made as follows: white collars, cuffs, and shirts, either linen or cotton; colored cotton clothes, usually sorted as to colors; woolen goods; white fabrics other than shirts and collars; and silks. It is evident that all of these groups could not be submitted to the same treatment; as for example, all could not be bleached by chloride of lime, as are the white cotton and linen goods. In order to simplify the present description, only the process employed in the case of white linen and cotton fabrics will be outlined and some of its chemical points will be discussed. The main differences between this and the other processes will then be mentioned briefly.

A representative outline of the "collar and cuff" treatment is the following:

[1] H. L. Jackson l. c., p. 644, note 2.
[2] W. S. Jevons, *Chem. News*, 21, 66.
[3] W. Spring, l. c., p. 644, note 2.

	Temperature.	Time of Run.
1. Cold rinse	Room temperature	5 min.
2. First suds	Brought gradually to boiling temperature in 10 to 15 minutes	25 min.
3. Second suds and bleach	Brought gradually to boiling temperature in 10 to 15 minutes	25 min.
4. Warm rinse	60–80° C.	5–10 min.
5. Warm rinse	60–80° C.	5–10 min.
6. Warm rinse and acid	40°	5–10 min.
7. Blue	40°	5–10 min.
8. Rinse	40°	5–10 min.
9. Rinse	40°	5–10 min.

Water Supply. Since water is used throughout the washing process, and is easily the most important agent of all, it may be well in the start to state the conditions which must be realized in a water supply, if good results are to be obtained. Hard water should never be used in the washer. If it is used in making the soap solution, or in the rinses, difficultly soluble soaps of calcium and magnesium, which are difficult to remove, are precipitated in the fibers. If not removed, they make the fabrics harsh, and when heated in the dryroom, or in the ironing machines, they decompose with the formation of yellow or brown substances. Experiments made by the writer have shown that larger quantities of soap and alkaline substances are removed by soft water than by hard, and the color of the finished product is uniformly better in the former case. This is contrary to the belief general among launderers, since when soft water is used, the rinse water continues to form suds even after several changes. This is not due, however, to a removal of less soap in this case, but rather to the fact that by the use of hard water the soap is changed into the above mentioned calcium and magnesium compounds, which do not foam on account of their slight solubility.

The softening must be carefully done, so that the water is left as nearly neutral as possible. Otherwise a larger quantity of alkali must be neutralized when the acid is added for the sour bath (6), which occasions an unnecessary expense. On account of the large quantities of water used, and since very few water supplies are suitable without treatment, a water softening plant of some kind should be installed in every laundry. It is not difficult to prepare a water which has from three to five degrees of hardness, and which is nearly neutral. An elaborate plant is not necessary —two tanks of suitable size to furnish the water needed are sufficient. Water may be used from one of these, while the precipitate in the other is settling out. The reagents may be mixed with the raw water by stirring with a paddle, with exhaust steam, or with compressed air. Very efficient plants which furnish a continuous supply of water are available. These have the advantage of requiring less ground space per given

hourly output of softened water than those of the above described intermittent type. Complete plants of the latter kind, which give perfectly satisfactory results, are also available. In the event that suspended substances are not carried down by the precipitate during the settling, coagulants, such as alum, may be added. A satisfactory procedure is to filter such waters through pressure sand filters which are designed for use in laundries. These filters give very good satisfaction, and are easily cleaned in a very few minutes by simply changing several valves. With an abundant supply of clear soft water good results are made much easier than is otherwise the case.

Cold Rinse. After the clothes are put into the machine, cold water is admitted and allowed to remain for about five minutes. The object of this cold water bath, to which a little soda ash or washing soda is frequently added, is to remove loose dirt, and also to dissolve albuminous substances, which would be coagulated if hot water were used at once. After about five minutes this action should be complete, and the water is discharged.

First Suds. Hot water is now run in, and the soap solution containing the alkaline substances, if any are to be added, is introduced. By admitting steam from the boiler, the temperature of the water may be raised to about the boiling point and kept there during the remainder of the run. The quantity of soap and alkali added is varied with the conditions, an average being sufficient to make the strength of solution about $\frac{3}{4}$ per cent in soap, and $\frac{1}{4}$ per cent soda ash. For a machine designed to wash 75 lbs. (approximately) of air dry clothes, about thirty gallons of this solution are required. After twenty-five minutes the solution is discharged. A very good feature would be to rinse at this stage in order to remove the dirty soap solution left in the clothes.

Second Suds. The second soap and alkali solution is generally made a little weaker than the first. The bleach liquor is added along with the soap, and the whole discharged after twenty-five minutes. The bleach most frequently used is sodium hypochlorite made from the calcium salt by treatment with soda ash. Electrolyzers for the preparation of sodium hypochlorite from common salt solutions by electrolysis are being introduced into some of the laundries. The bleach liquor produced by them is similar in action to that made from bleaching powder and soda ash, as would be expected. The former contains more sodium chloride, but is more easily prepared neutral than the latter. Enough of this bleach solution is added in the washer mentioned above to yield from 50 to 70 gms. of available chlorine. Many colored substances are removed by being oxidized by the hypochlorite, the resulting colorless substances being taken away by the soap and alkaline substances added. Many tests have shown that the available chlorine is all used up in from ten to thirty minutes under the conditions it is used, the difference in time depending on the rate at which the solution is heated. This fact

is of importance to launderers, and explains the appearance of a yellow color in certain lots of clothes. The yellow color is caused by the formation of a colored substance through the action of alkalies with oxycellulose, the oxidation product of cellulose and the hypochlorite. The persistence of this color becomes possible when the available chlorine is all destroyed before the solution is discharged. The yellow compound is destroyed by hypochlorites, also by acids.

The most harmful part of the washing process, as it is ordinarily conducted, is unquestionably the bleaching. This has been shown in a number of ways.[1] Independent series of collars have been treated each by a separate one of the operations, e.g., soap, alkali, soap and bleach, acid, etc., and then starched and ironed. Those collars of the bleach series broke much sooner than the others—seven to nine treatments being an average for the bleached collars, and twenty-five for a series washed in hot water and employed as a check. A determination of the breaking strength of cotton threads has shown the same thing.[2] Threads which broke originally at 1725 gms. had their breaking strength decreased to 100 gms. when treated twenty times, using the larger quantity of available chlorine mentioned above.

Acid Rinse. The purpose of the acid solution is the neutralization of all alkalies not rinsed from the goods. The blues which are used to counteract yellowness in the clothes are basic aniline dyes, and are decomposed by alkalies. Sufficient acid is added to neutralize the alkalies and to leave a slight excess—usually less than N/50 with respect to the acid. The acids used are acetic, lactic and oxalic. The first two have the advantage of being very weak acids and consequently do not attack cellulose readily, even when their solutions are concentrated. Oxalic acid is considerably stronger than these, but is extensively used because it removes iron stains, on account of the formation of complex iron-oxalate anions. The action between acid and cellulose is not marked so long as the acid remains dilute, as is the case while the fabrics are in the machine. However, any acid which is not rinsed out becomes concentrated when the articles are placed in the drying room, or passed over the heated rolls of an ironing machine. Since the acid is not used up during the reaction, a small quantity of this dilute solution is able, after concentration, to hydrolyze considerable cellulose in a relatively short time.

Tests were run on series of cotton threads as follows: the threads were dipped into N/50 solutions of sulphuric, hydrochloric, acetic and oxalic acids. They were then run in an extractor without having been rinsed, and dried for twenty minutes at 100° C. This operation was

[1] Unpublished results by writer.

[2] Series of 100 threads each were used in order to obtain a reliable mean value. Duplicate determinations show that the mean thus obtained is accurate within the limit of the other experimental errors.

repeated ten times, rinsing with distilled water between treatments in order to remove the acid left. The following results were obtained:

Original breaking strength	1725
Acetic acid series	1520
Oxalic acid series	265
Hydrochloric acid series	<20
Sulphuric acid series	<20

Boiling a series of threads in N/50 oxalic acid solution for three hours caused a decrease to 1250. It will be seen that if oxalic acid be used and no rinse follows the blue solution, this operation is one of the most harmful. A series of collars treated in this acid solution with no sub-

Fig. 326.—Extractor—a Centrifugal Machine.

sequent rinse were starched and ironed, with the result that after eight to ten times all of them had broken.

Very frequently all of the alkali is not neutralized, and when this is the case the blue does not set evenly. Besides, the alkali causes a conversion of starch to dextrins and glucose when heated in the ironing machine. These substances decompose at the high temperature into yellow products, a fact which often explains the production of poor work under these conditions.[1] From the washer the articles are placed in large centrifugal machines, Fig. 326, which are driven at a speed of 1700 to 2000 revolutions per minute. This removes most of the water in about fifteen to twenty minutes, so that the fabrics are in a suitable condition to be starched at once.

Starching. Starching is done in machines which rub the solution into the fabric. The starches most extensively used are the so called thin

[1] Skinner, *J. Am. Chem. Soc.*, 27, 165 (1905).

boiling wheat and corn starches. They have been partially converted by acids, according to the processes given in Chapter XXXVIII, until they form a relatively thin solution upon being boiled with water. The solution is used hot, from 65–70° C., since at this temperature a solution of the strength which gives the right weight and pliability to the finished fabric penetrates most readily (approx. 100 grams starch per liter).

After being removed from the starcher, collars and cuffs are taken to a table where the excess of starch is wiped off, first by rubbing with the hand and then with a piece of cheesecloth. Care is taken to get

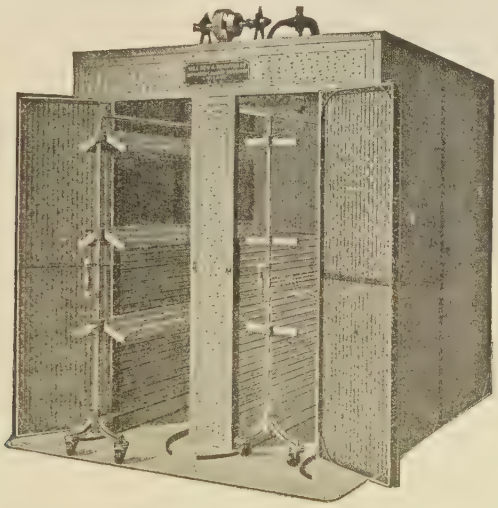

Fig. 327.—More recent dry rooms are provided with an endless traveling belt, to which the fabrics are fastened. The speed of this conveyor is regulated so that the articles remain in the dry room about half an hour. Upon emerging from the dry room, each piece is automatically released, and falls into a basket.

the starch worked into the fabric so that the plies will be held together after ironing.

Since the starcher leaves too much water in the pieces to allow of their being ironed at once, it is necessary to dry them. This drying is done in specially constructed drying rooms, Fig. 327, which are heated by steam pipes. Ventilation is provided by a system of fans, for the air must be changed frequently in order to remove the large quantities of water quickly. It is not practicable to carry the drying to the extent just suitable for the ironing, so the moisture is removed as completely as possible. It is then necessary to dampen again and this is done by one of several methods.

Dampening. The method used in most small plants, and in many larger ones, is to wrap the collars in damp cloths. Experience teaches the conditions necessary to produce the proper amount of dampening.

Machines which work by carrying the articles to be dampened between moist padded rolls are used also.

Ironing. The ironing machines for collars and cuffs, Fig. 328, consist of large gas heated metal rolls, which are padded with cloth, between which the pieces pass. On account of the difficulty of regulating the flow of gas and air to the burners, the temperature of the rolls varies within quite wide limits, and this has a tendency to make the finish of the work irregular. The gloss on the finished pieces is controlled by the friction applied on passing the rolls. Steam heated machines have been perfected in the last few years, and have the advantage of giving more uniform results, since the steam pressure in the boiler is all that needs to be regulated in order to give a certain temperature to the rolls.

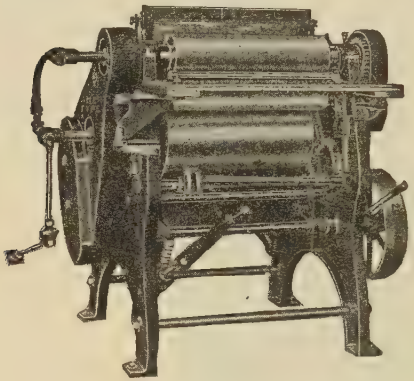

Fig. 328.—Collar and Cuff Ironer.

Since collars and cuffs are ironed flat, many of the collars must be turned and shaped. To prevent undue strain during the turning, the seam is dampened by machines, various types of which are available. The shaping is also done by machines, in which the moisture introduced when the seam is dampened is removed, and in some cases the edge of the collar is ironed.

Colored Fabrics and Pieces which Require no Starch. Colored articles cannot be treated with as strongly alkaline solutions as those mentioned above, and the bleaching liquor must also be omitted. It is a common experience that colored articles which are sent to the laundry last much longer than white ones.

For white cotton and linen articles that need not be starched, the usual practice is to take them directly from the extractors to an ironing machine, called a mangle, Fig. 329, or flat work ironer. These machines have a number of steam heated rolls, between which the pieces pass. They are constructed large enough to iron sheets and table cloths on a single passage between the rolls.

Wool and Silk. Woolen and silk articles must not be treated with alkalies on account of the corrosive action these exert. The chlorine bleach is also dispensed with, since hypochlorites render wool and silk harsh and weaken the fibers very markedly. In case a bleach is necessary, hydrogen peroxide, sodium perborate, or sodium hydrosulphite may be used. All of these substances are obtainable now at a price which permits their use for bleaching wool and silk.

For the ironing of bosoms and cuffs of shirts and plain shirt waists, special machines are used. These have a movable cloth-padded board, upon which the shirt is fastened and caused to pass under a heated roll. Steam heated machines which operate by simply pressing the articles between heated surfaces, are being introduced extensively, and possess the advantages mentioned in the case of other steam heated apparatus. The body and neck bands are ironed by specially constructed machines, which work on the principle of the others already described. Much of the work on fancy articles must be done by hand, and the use of electrically heated irons is facilitating this operation very much.

Cleanliness is very essential in the laundry. All walls must be plain, and all overhead machinery must be arranged so that dirt and oil are not allowed to fall on the clothes.

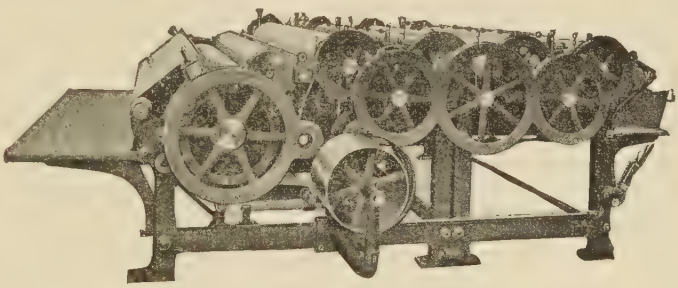

FIG. 329.—Mangle or Flat Work Ironer.

Another field for chemistry in the laundry is presented in the analysis of supplies furnished by dealers. Adulterations, such as excessive amounts of water in soaps and starches, talc and water glass in soaps, and common salt and carbonate in caustic soda may be detected, and great savings thus be effected.

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CHAPTER XXXI

ESSENTIAL OILS, SYNTHETIC PERFUMES AND FLAVORING MATERIALS

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Historical. The history of perfume materials dates back to the dawn of civilization on the banks of the Indus, the Tigris and the Nile. Sanskrit writers in India two thousand years ago frequently mentioned perfumes.

As the origin of the word perfume shows (Latin *per-* through, *fumare-* smoke) the first perfumes were used in the form of incense, forming a part of religious worship, from the earliest to the present time. It is interesting to note that some of the oldest perfume materials known are still being used. For instance, in ancient India the sacred fires in the temples were perfumed with kusa or kus, the fragrant root of cus-cus or vetiver, a native grass. This odor is a constituent of many of the present popular perfumes, as in the type of azurea bouquet and the many variations of Oriental bouquet perfumes so successfully marketed under many different names. Confucius, the Chinese philosopher, mentions the use of perfumes in China in his works, written about 480 B.C. Incense is the most popular form of Chinese perfume to the present time, as shown by the so-called joss sticks or incense sticks, which are imported into this country in large quantities. That perfumes were well known in Babylon and Nineveh is shown by perfume flasks which were excavated by Layard at Nimrud below Nineveh, curious ornamented containers of porcelain and glass, with cuneiform inscriptions. In Egypt perfumes were lavishly used in the form of incense, as fragrant ointments and oils, in daily life as necessary toilet accessories, as part of the religious ceremonies and in the preservation of dead bodies, which was therefore called embalming. In early Greek and Roman writings, as well as in the Bible, we find frequent references to perfumery and incense. All these ancient perfumery materials consisted of crude drugs, flowers, herbs, aromatic gums, resins and woods of the Orient, including many of the fragrant flowers which are utilized in modern perfumery. The earliest method of extracting the odorous constituents from the crude material consisted of macera-

[1] Deceased.

ation in oil. The ancients knew that fats have the power to take up and hold the perfume of substances with which the fat is brought into contact. This old process is still followed in southern France, where flowers are macerated in oil to produce the so-called "flower pomades." The Greek writers Appolonius and Theophrastus mention many of the flowers and materials found in commercial application up to the present time, among them iris or orris, lily, rose, violet and labdanum, an Oriental gum, the active principles of which have lately come so prominently into use as a fixative in the manufacture of fine modern perfumes. Inasmuch as all the materials first used—that is, resins, barks, woods, herbs, flowers, etc., contain the fragrant principles in only very minute proportions, great bulk had to be used, and the next step forward was the discovery of steam distillation. The forerunner of this method was the crude attempt of the ancients, who noted that the steam from a boiling caldron had the odor of the contents and who placed wool over a vessel in which for instance, cedarwood was boiling in water, and then squeezed the wool in order to obtain the condensed volatile oil.

While the Egyptians were said to have been acquainted with the principles of distillation, nothing positive is known. Avicenna, a famous Arabian physican and writer of the tenth century, is said to have perfected the process, and the Arabian word alembic (meaning *al-* the, *embic-* still) is used even at present. It is likely he produced the first rose water and rose oil by steam distillation, a commercial process by which oil of rose is now made in Bulgaria, Persia and France.

In time it was found that the odor of most substances which are useful in the perfumery industry is due to a certain class of bodies designated under the terms of essential or volatile oils. Some of these may be obtained from the raw materials by steam distillation, that is, steam is passed through a mass of the flowers, herbs, seeds, woods or barks, which frequently must first be finely subdivided or ground and on cooling the steam, the oil, which is volatile with it, separates from the condensed water. In a few cases, as with rose and orange flowers, the condensed water is likewise salable, because it contains the more soluble portions of the flower odor, or odoriferous decomposition products of some of its constituent bodies in solution, although only in infinitesimal quantities. Steam distillation is commercially used in producing a number of the essential oils, for instance, anise, cassia, clove, geranium, lavender, linalœ, neroly, orris, peppermint, rose, sandalwood, turpentine, wintergreen, and ylang ylang. From the small alembic used in former times to a modern still which has a capacity of many thousands of gallons, there has been no change in the principle.

Crude Distillation. Many of the essential oils are distilled by unskilled natives in the various countries, and the layer of water is usually heated by direct fire placed under the still. It is now well known that this both decreases the yield and produces an oil inferior in quality, as it subjects

the material to the saponifying or hydrolyzing influence of hot water and some small particles of the substance being distilled are sure to adhere to the bottom of the still, where they scorch, and contaminate the distillate with a burnt odor.

Modern Distillation. In modern factories steam is generated in a boiler and passed into the still at various degrees of pressure. Usually the still is also heated either by means of a steam jacket or by a closed steam pipe placed inside the still, so as to prevent much condensation of the steam in the still. The degree of fineness of the charging material, the pressure, and therefore the temperature of the steam, the speed of its flow and numerous other working points must be adapted in each case to the apparatus in use, as well as to the substance that is being distilled and the product that may be expected.

Oil Content. The volatile oil content in plant material differs enormously. For instance, cloves contain from 14 to 20 per cent of oil. As a rule, however, most of the plants contain less than 5 per cent and in many cases only the merest traces of essential oil. It may be mentioned that it requires from 3500 to 4200 pounds of rose flowers, according to season, to obtain one pound of pure rose oil by steam distillation. This, however, is not a true indication of the amount of perfume oil actually present in the flowers. *Steam distilled oils never contain all of the perfume constituents present in the plant.* Some of these have such a high boiling-point, that they do not pass over with steam, others are decomposed into other derivatives and others pass into the water. As an illustration we may consider Oil of Rose. The distilled oil seldom contains more than 1 per cent of phenylethyl alcohol. The oil obtained by extraction contains from 50 to 60 per cent of this alcohol, which is one of the principal odoriferous constituents of the rose water of commerce.

Steam Distillation. *Hence oils obtained by steam distillation cannot be expected to have the exact odor of the flower or material.* We must remember that the odor and taste of all natural products are due in almost every case to a combination of a number of chemical bodies and it is only when these chemical individuals are assembled in the right proportion and combination, that the odor of the flower or material will be duplicated. Many of these chemical bodies are extremely sensitive to heat, which either destroys them or changes the odor completely, others are esters which are hydrolyzed by the action of steam and heat and many plants contain bodies which upon heating act to a greater or less extent on the other constituents. Consequently, steam distillation has its limitations and other processes must be utilized to extract the active principles desired.

Scientific research has also proven that many plants contain bodies of very high boiling-point, which influence the odor considerably and which are at best only incompletely volatilized by steam distillation and frequently remain entirely in the residue. Some of the valuable constituents do not

exist in the plant as such, but are combined as glucosides. As instances we may mention the odor of cumarine, so apparent in mown grass and entirely different from the odor of the field, and the odor and flavor of vanilla beans, which is developed in the fruit on ripening, but to a far greater extent when the bean is skillfully cured.

Expressed Oils. That squeezing the rind of some fruits left a fragrant oil on the hands must have been early observed. It is still the method which gives the finest oils of the citrus family and is the present commercial method of obtaining the oils of lemon, orange and bergamot. As cheap labor is available in Sicily, where these oils are made in quantities, and the pulp of the fruit is worked up for citric acid, the price remains quite low, although the method is slow and tedious. The peel is manipulated, crushing the oil cells and the oil is absorbed by a sponge, which is then squeezed and the oil filtered for the market. Machines have at times been tried to take the place of hand labor, but none of them have been found commercially satisfactory, excepting to a limited extent for the regularly shaped bergamot. The citrus oils will illustrate the damaging influence of heat and steam on odors in general, as steam distilled oils totally differ in odor from the fruit and have but little commercial value.

Macerating Process. We have already mentioned the process of macerating flowers in warm oil or fat, a method by which the modern flower pomades are produced in southern France. After the oil or fat has absorbed the odor of the flowers, it is strained off and a fresh lot of flowers added. This process is repeated a number of times, according to the strength of pomade desired.

Enfleurage Process. It was found, however, that even the slight heat necessary in the macerating process is sufficient to destroy some of the more sensitive constituents of some flower odors, and the cold enfleurage process resulted. Here a layer of fat is placed on a plate of glass, fresh flowers are sprinkled on it and after the fat has absorbed the odor, they are replaced by more flowers and this process is repeated until the fat is saturated. This process is especially adapted to flowers like the jasmine blossom, which is known to produce perfume for some time after it has been picked and a much better yield results than when the flower is immersed in hot fat, which immediately stops the production of more flower oil by the blossom.

Flower Pomades. This flower pomade, obtained either by maceration or by the enfleurage process is then washed with alcohol, which extracts from the pomade the odorous substances, which this has absorbed from the flowers. Here again the same objection of large bulk presents itself, as the fat absorbs only a very small proportion of the fragrant constituents. Then there is another more serious objection to the flower pomades that are obtained by maceration or enfleurage, namely, that the fats employed (usually lard or tallow) will turn rancid in time, and, further-

more, even the best quality of neutral fats contain a small proportion of alcohol soluble constituents (traces of alcohols, ethers, aldehydes, ketones and esters belonging to the fatty series) which impart a greasy odor to the spirit used for washing the pomade. This greasy by-odor (and, where pomades have been kept for a long time, the decidedly rancid by-odor) seriously interferes with the flower odor proper.

Volatile Solvents. These objections have led to the more modern process of treatment by volatile solvents. Petroleum ether, carbon tetrachloride, chloroform and other volatile bodies have been used for this purpose. These solvents in passing through a layer of flowers or materials, dissolve the odorous constituents, together with the plant resins, coloring matter, waxes and other substances present, which are soluble in the solvent utilized. By then distilling off the solvent at a low temperature usually in a partial vacuum, the odorous bodies, with the impurities mentioned, remain in the residue. As the yield from different flowers varies greatly, various quantities of wax, paraffine or some liquid odorless ester are usually added to reduce the cost and in order to market the different odors at the same price.

Flower Concretes and "Absolutes." By this method the so-called "flower concretes" are made in southern France. This process has recently been improved again by eliminating from this concrete the alcohol insoluble portion. The concrete is treated with alcohol, thus extracting only the alcohol soluble constituents and the alcohol distilled off, which gives a final product, marketed under various trade names, but usually called "absolute flower concrete" or "absolute flower essence." In another process, the waxes naturally present are precipitated, separated, and the solvent then evaporated in the usual manner. Other of these essences are obtained by washing the pomades and distilling off the alcohol. These, of course, are subject to the same objections as the pomade, as the fatty by-odors, eliminated by the volatile solvent process, are present in same. *All these so-called "absolutes," however, are far from absolute in practice,* because they still contain quite a large proportion of various odorless constituents and coloring matter present in the plant. Furthermore it is quite a common and well-known commercial practice to add to these so-called "absolutes" odorless esters or chemical bodies, with the two-fold object of making the products more soluble and principally of reducing their cost, thus compensating in a measure for the fluctuating yield due to season and the ever-changing cost of production, often due to speculative influences.

Adulterations. Owing to the high value of many essential oils and perfumery products, they are frequently adulterated. In former years this was very crudely done by adding paraffin, fatty oils in varying proportions, alcohol, and other crude diluents. As science progressed, however, and made many methods available for testing the purity of these products, these clumsy adulterations have gradually disappeared from

the market. But their place has been taken by much more dangerous adulterants, which frequently can be found only by careful analysis. Consequently the old methods used for the detection of added alcohol by washing with water and noting shrinkage in volume, or by testing with certain aniline dyes which are insoluble in essential oils but dissolve if even traces of alcohol are present, and other crude testing methods, are of but little value nowadays. Neither is the old empirical method, to ascertain whether the oil leaves a grease spot on paper on evaporation, of value—some oils like bergamot, rose, etc., contain waxlike fatty bodies, which will produce a greasy stain. Then again methods of distillation are being constantly improved and constituent bodies of high boiling-point, formerly lost, are now often present in the modern product. Only the ignorant native and the veriest novice employ the old adulterants we find so frequently mentioned. Many of the oils are now so skilfully adulterated that it requires great care, and all the physical and chemical constants of a sample must be considered together, to determine its purity.

Solubility. Most of the essential oils are soluble in alcohol, and by noting the volume of alcohol necessary to effect complete solution comparative data may be obtained, which can be made more exact by employing alcohol of different strengths.

Specific Gravity. This usually ranges from 0.850 to 1.100. Oils rich in terpenes (which have an approximate S.g. of 0.800) mostly approximate 0.850 to 0.900. Since the advent of terpeneless oils the terpenes removed from these have become dangerous adulterants. Their addition in appreciable quantity, which lowers the gravity, is often concealed by adding some ester of high gravity like benzyl benzoate (S.g. 1.12). S.g. can be most conveniently and quickly ascertained by means of the Westphal S.g. balance, if the size of the sample makes this possible.

Boiling-point. This is of but secondary value as *all essential oils are mixtures of many different chemical bodies,* which differ widely in boiling-point.

Fractional Distillation. If the size of the sample makes this possible, this is often one of the best methods, as various adulterants can be detected to much better advantage in the different fractions. To prevent decomposition the product should be fractionated in as low a vacuum as possible. 1 or 2 mm. can be easily obtained, when distilling from a liter flask by using modern laboratory equipment.

Optical Rotation. The polariscope will give useful figures with many essential oils. It must be remembered, however, that some variations are unavoidable, as the same plant owing to climatic or soil conditions will in different countries yield an oil differing somewhat in rotation.

Solidification Point. The temperature at which some oils congeal proves an important indication of their purity. For instance, oil of anise is tested by this method.

Aldehydes. Some oils contain a large proportion of aldehydes; cassia oil—cinnamic aldehyde; oil of bitter almonds—benzoic aldehyde or benzaldehyde, etc.; 10 to 15 cc. of the oil are shaken with warm sodium bisulphite solution. The aldehyde goes into solution, and by measuring the oil not absorbed the percentage can be quickly calculated. By using a flask with graduated neck and adding sufficient solution to bring the oil into the neck, the percentage can be instantly read. In some cases it becomes necessary to further prove the identity of the aldehyde. Samples of phenylacetic aldehyde, submitted frequently for examination by the writer, were found to contain a large proportion of benzaldehyde, which has a totally different odor and is worth only a small fraction of the cost.

Phenols. These are estimated by a similar method as the aldehydes, using a 3 to 5 per cent solution of sodium or potassium hydrate in water. Oil of cloves is thus tested for percentage of eugenol.

Acid Number. This is ascertained by titration and represents the number of milligrams of potassium hydrate necessary to saturate the free acid in 1 gram of oil. While the percentage found is usually small, representing chiefly traces of formic and acetic acids present in many oils, it should be ascertained in order to deduct the amount in the following test.

Ester Test. This is one of the most important tests in connection with essential oils, as so many of these owe their value to the percentage of certain esters present. About 2 grams of the oil are dissolved in alcohol and cooked in a flask with reflux condenser with about 20 cc. of semi-normal potassium hydrate solution for one hour. The number of milligrams of potassium hydrate required to neutralize the acid present in the form of esters in one gram of oil as ascertained by titration, is called the ester number. From this the proportion of ester present can be easily figured. In the case of monobasic acids it is merely necessary to multiply the ester number by the molecular weight of the ester and divide by 560. For instance in a sample of bergamot oil the ester number found is 100. Multiplying this by the molecular weight of linalyl acetate ($C_{12}H_{20}O_2$) = 196, and dividing by 560 we get 35 per cent of ester.

Alcohol Percentage. This is usually obtained after the free acid and ester number have been ascertained. About 10 grams of the oil are boiled for one hour with 10 to 12 grams of acetic anhydride and 2 grams anhydrous sodium or potassium acetate, using a reflux cooler. The oil is then neutralized, washed, dried, and the ester number is found again by saponification as in the previous paragraph. By deducting the acid and ester number, we get a figure which corresponds with the percentage of free alcohol which was present in the oil. The percentage may be easily calculated from the amount of acetyl ester formed in this process. This gives accurate results with primary alcohols like benzyl, phenylethyl, cinnamyl, geraniol, etc., but only approximate data can be had with

linalool and terpineol as these form esters only with difficulty and never quantitatively.

With these methods most of the important constituents of oils may be determined. When a number of allied esters, alcohols or aldehydes are present their identification becomes very complicated and then requires special processes, often very tedious and intricate in character, which task the skill of even an expert analyst.

Modern Sophistication. Many items have been added to oils in recent years, specially selected so that the values shown on analysis would be fictitious. A whole series of esters has been artificially produced for no other purpose than to serve as adulterants. The odorless ethyl oleate and the glyceryl esters of acetic acid are freely and openly offered by certain European chemical houses as "*very useful products, which are very widely used.*" They can serve no useful purpose, but to give bergamot, lavender, and other oils a fictitious ester value. Many of the modern sophistications are exceedingly difficult to detect. For instance, while it has been well known for many years that the peasants in Bulgaria frequently sprinkle the rose petals before distillation with either geranium oil or geraniol, more dangerous adulterants have found their way into rose oil, for instance, mixtures of the alcohols geraniol and citronellol, normally present in the rose flower, made so skillfully that their detection in the finished product becomes almost an impossibility. Consequently, many of these oils are valued solely by their odor, when chemical tests fail.

Constitution of Perfume and Flavoring Materials. The complex nature of these has only been properly studied in recent years.

As organic chemistry progressed and methods were found to identify and isolate from the natural materials various constituents present in them, *it was found that almost without exception every odorous material in nature is a compound.* Quite frequently materials contain chemical substances or individual chemical bodies belonging to entirely different series and in no way related to each other. Some of these substances are extremely sensitive to heat and chemical reagents, and therefore their isolation and identification present the greatest difficulties, but it is just this *combination* of different chemical individuals to which the fine odor of almost all flowers, plants, and other materials is due. As a rule all of the definite chemical constituents, when used alone, give harsh odors. The delightful flowery aroma is only developed when they are present in proper combination, as they exist in nature, or as the skill of the chemist may combine them. This has led to commercial synthesis of the finer flower products.

Synthesis. The collaboration of thousands of chemists throughout the world, for some years past, has made a new industry possible, the industry of synthetic perfume and flavoring materials, which has come to the assistance of the manufacturer, by producing the same substances at a saving in cost, and by overcoming the frequent price fluctua-

tions of the natural materials, war conditions excepted. Many of the substances which naturally exist in the plants or materials may be manufactured chemically from other sources. Let us select one example, the jasmine flower, which is so invaluable to the perfumer. If we submit the so-called " absolute jasmine flower essence or concrete " to a further process of purification, to eliminate the inodorous constituents present in it, we finally obtain a jasmine essence, which contains from 60 to 65 per cent of benzyl acetate. The absolute product containing this percentage, as made from the blossom, represents an actual expense of about $180 to $260 per pound, according to season. But we can obtain benzyl acetate chemically from an entirely different source at much less expense. If we take toluene (methyl benzene), one of the constituents of coal tar, and treat it with chlorine, we obtain benzyl chloride. If we now exchange the chlorine for the acetyl group, we get benzyl acetate, which when highly purified, is identical with the product as it exists in the flower, and is marketed absolutely pure at about one hundredth the cost. This not only represents an enormous saving in the industry, but makes it possible to use raw materials frequently for various purposes, where the natural product was not heretofore available, owing to its high cost. But while this synthetic benzyl acetate is absolutely the same definite chemical body as found in the flower oil, it is not jasmine. What we know as jasmine is nature's combination of many different constituents and we do not get what we call a jasmine odor until we produce each of these constituents and assemble them in the right proportion. By suitably changing the proportion of these constituents we can obtain new odor effects, different shadings of the same flower odor. Flower oils are usually exceedingly complex. Often more than one hundred different chemical bodies must be produced and assembled to duplicate an odor known as " a simple flower odor " because each of these bodies is present in the plant and we cannot get the same odor effects unless we unite the same constituent bodies.

New Perfume Materials. A great many chemical substances have been found which have most delightful odors and flavors and which, to our best knowledge at the present time, do not exist in nature as such—at least, they have not been isolated from the natural materials. Many such substances are now commercially manufactured and have enriched the industry with a variety of new raw materials, which enables the manufacturer to produce entirely new effects. Many years ago, when the industry was in its infancy and purification processes had not developed to the present state of perfection, the synthetic materials were merely used for the purpose of diluting and cheapening the more expensive natural products, but this has wholly changed during the last few years. The synthetic materials of to-day are successfully utilized in goods of the highest grade, and many odor and flavor effects would be impossible without them.

Purification Processes. At the outset, we must emphasize, however, that quality is the foremost consideration in every perfume or flavoring material. Traces of by-products sometimes present, not large enough to be found by chemical tests, will often seriously interfere with the odor and flavoring value. Modern science has made many methods available by which products may be purified by either chemical or physical methods, so that we can obtain these bodies in a state of absolute purity. Among the chemical methods, we refer to the extraction of aldehydes or ketones by means of bisulphite, semicarbazide, phenylhydrazine and other reagents and the extraction of alcoholic bodies by means of the acid phthalic esters. As one of the most valuable methods of separation we mention the process of vacuum distillation, which has been greatly simplified and perfected during the last few years. Many of the most sensitive constituents of plant odors may be distilled unchanged at a very low vacuum. Scientific advances in engineering practice have so perfected vacuum pumps that substances can be distilled commercially by reducing the ordinary air pressure to an absolute pressure of from 1 to 4 mm., at which point a great many substances are distilled commercially without change which would be decomposed if distilled at ordinary pressure. Furthermore vacuum distillation lowers the boiling point enormously, in many cases more than 100° C., thereby reducing heat changes to a minimum, and by carefully repeating the vacuum distillation several times, eliminating in each case the fractions containing the impurities, bodies may be produced in a state of almost absolute purity.

Chemical Treatment. While steam distillation will continue as one of the popular processes of obtaining from some of the plants or crude materials the active principle, the steam-distilled oil can very often be greatly improved by chemical treatment, combined with a proper vacuum distillation process. The natural oils contain many substances which are detrimental to the odor, and can readily be eliminated, in that way producing an article which has a higher perfume value and a much finer odor. As a practical illustration, let us for instance take Mexican linalœ oil, which has a rather harsh and crude odor, owing to the impurities present in it. By chemical treatment and repeated vacuum distillations we can readily obtain from this oil the valuable terpene alcohol linalool, of which we will speak further on, a product that has a very fine flowery odor and can be safely used in even the highest grade products, where the normal essential oil would be entirely out of the question.

Chemical Constitution. Among the many chemical bodies which contribute their share to the odor or flavor of materials valued in the industry, we find representatives of both the aliphatic or fatty series and the aromatic or benzene series. The great majority consists of merely three elements, carbon, hydrogen and oxygen. A smaller number of compounds, some of which are important, contain nitrogen—for instance, different varieties of artificial musk and amide bodies, derivatives of

the benzoic acid series, like methyl anthranilate, one of the most valuable constituents of orange flower and many other flower oils, and the methyl ester of methyl anthranilic acid or dimethyl anthranilate, which while present usually only in traces, contribute greatly to the flowery sweetness of many of nature's most valued blossoms.

Chemical Methods of Production. The reader will doubtless be interested in the chemical methods used in producing on a commercial scale, by synthesis, the bodies which occur in nature. This however involves so many chemical processes that the subject can only be briefly treated, inasmuch as all the methods of modern organic chemistry are utilized. It may be said for the information of the student that many of the reactions commercially utilized are exceedingly complex, because the substances in most instances have to be built up gradually and the intermediary products purified, so that it often requires weeks and months of work to perfect one of the chemical bodies to which a particular flower owes part of its odor. In considering the best known constituents which find commercial application, we shall in a few instances, by way of illustration, mention the process used in their manufacture.

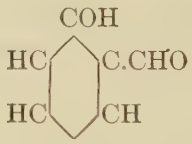
Stability. After producing and purifying the various constituents comes the equally important problem of assembling them in the right proportion, so that they will not only impart the exact odor of the blossom, but will prove commercially stable. Many of these bodies cannot be preserved as individuals—they either oxidize or resinify on exposure to air or light or are condensed into high polymers, which are odorless, therefore of no value and often insoluble in the common solvents. As an instance, let us consider styrol or styrene, which in traces, helps to give life to many flower oils, yet which is of no value alone, as it changes very quickly into meta-styrene, a glassy, horn-like inodorous body, insoluble in alcohol, oils, and all ordinary solvents. Styrol is interesting, as it is one of the few hydrocarbons of value to the industry, having the chemical formula $C_6H_5CH{:}CH_2$. Berthelot isolated this product from coal tar in 1864, Von Miller from storax, but it remained merely a chemical curiosity, and had not found commercial application until recently, as it was discovered that it would change readily on standing, even when kept in the dark and in sealed tubes, consequently it must be added to flower oils while perfectly fresh as soon as produced in order to preserve its odor value. Even when kept over night it will often polymerize almost completely. Hence Styrol is a good example of a large class of substances, which when added to perfume oils in very small proportion produce a natural freshness, yet which cannot be marketed by themselves, owing to their instability, in the undiluted form.

Commercial Synthesis. The student of industrial chemistry must always keep before him the question—"Is a process feasible—can it be commercially applied?" Owing to statements that have found their way into print during the last decade, many chemists have an idea

that by duplicating a few of the major constituents of an odor, they can produce the same effect; but this is false. How often has the writer been approached by a student, and sometimes by chemists that have followed organic chemistry for many years, who have expressed their disappointment that, for instance, terpineol would not produce a lilac perfume, or that benzyl acetate would not produce a jasmine! Here we must remember the complex constitution of materials produced in nature's laboratory. Take for instance benzyl acetate, the item last mentioned—it is well known that in plants, where esters of the acetic acid series exist, esters of allied acids will also be present, though in smaller proportion, and, as a rule, we find a mixture of the formates, the acetates, the propionates and sometimes traces of even the higher acid esters in combination with the particular alcohol. Then the alcohol itself, as a rule, does not exist alone. As an illustration, we mention bergamot, which popularly has been supposed to contain only linalyl acetate as the active constituent, until recently, when it was conclusively proven that not only the esters of linalool, but of several of the allied terpene alcohols, are present in varying proportion, and unless the chemist who desires to apply synthesis commercially, produces all these different compounds and combines them in approximately the proportions in which nature combines them in the plant, he cannot hope to compete with the products made from the blossom, flower or fruit.

Effect of Minute Traces of Compounds. Scientific investigation has shown that the finest and most valuable odors in nature are exceedingly complex. We may find that four or six or ten constituents are present in appreciable proportion, and yet if we combine these the product does not satisfy. The reason is easily perceived—we have ignored the traces of substances present, which sometimes are infinitesimal, but which have such a powerful odor that their addition immediately changes a harsh-smelling compound into a most delicate and flowery product that can be utilized in goods of the highest grade. The higher fatty aldehydes and alcohols, the use of which is but little understood by the average manufacturer of to-day, will serve as an example. Sometimes two or three drops of one of these substances to the gallon is sufficient to create that life-like touch, or to bring out the charm of the blossom odor to perfection. Some of the most charming plant and flower odors have not as yet been duplicated synthetically, but chemists all over the world are working on these problems In the course of time, all of the odors will be available, but it must be remembered by the student that he should not be discouraged if he does not get results immediately. It often requires years of painstaking study, in order to ascertain the proportions of individual constituents that will prove of the greatest value and in many cases from eighty to one hundred and even more of these constituents are present in a single flower product, although some of them may be present in traces only.

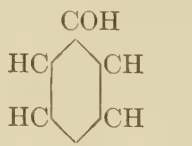
Odor Groups. A great deal has been written about certain odor groups, so called, which are supposed to give definite value when present in a chemical compound. Among these have been mentioned the phenol group OH, the ketone group CO, the aldehyde group CHO, the primary alcohol group CH_2OH or the alkyl radicles as for instance the methyl group CH_3, the ethyl group C_2H_5 and others higher in the series. This is however mere speculation, notwithstanding statements made to the contrary. We should confess that we know very little as yet as to why and under what conditions these groups produce such decided changes in the odor or flavor of a substance, because we have many representative examples, where individual chemical bodies contain either one or several of these groups and yet have practically no odor or flavor. Consequently, we must disagree with the published statements that there is such a thing as advance estimation of a product by knowing its chemical formula. We do know that sometimes the slightest change in a formula converts a highly odoriferous substance into one that is odorless, and vice versa, but we do not know enough about the subject to formulate any theories. In this connection it will be interesting to note that with products belonging to the benzene series, the grouping of the different radicles on the ring, often produces important differences in the physical constants of the chemical body. For instance, let us mention as a typical example, ortho-oxy-benzaldehyde.



Ortho-oxy-benzaldehyde ($C_7H_6O_2$)
(Salicylic Aldehyde)

Here we have the phenol group OH and the aldehyde group CHO adjacent to each other on the benzene ring. It is an oil which has a very powerful odor, is found in traces in many plants, and serves as a raw material for building up by synthesis other compounds which are valuable.

Let us compare this with the isomeric para-oxy-benzaldehyde, which has exactly the same formula, only here the phenol group is in the para



Para-oxy-benzaldehyde ($C_7H_6O_2$)

position,—that is, opposite to the aldehyde group on the benzene ring. This is a practically odorless white solid, having a melting-point of 116° C. This shows that the theory of odoriferous groups works very

well on paper, but does not apply in practice, because here we have a substance that contains two of these so-called odoriferous groups, yet this substance has practically no odor, although it can serve as a basis for building up other products by synthesis, as explained further on.

Fixatives. Some of these products which have but little odor are of value to the industry, because they are substances the perfumer calls "*fixatives.*" In the plant, the perfume is produced continuously in mere traces and is given off in infinitesimal quantities to the surrounding atmosphere. When we, however, isolate these bodies to which the odor is due, and have them in concentrated form, their odor as given off is too intense and when we take a small amount of this concentrated material and allow it to evaporate, the odor will not last as long, because it will evaporate more quickly than in the plant and, furthermore, the odor being so concentrated and intense, will not be as sweet or as flowery. If we, however, use with the material various substances known as fixatives, the odor is made less volatile. The perfume is only given off in small quantities at a time and we therefore duplicate the conditions existing in nature. In former times, ambergris, musk, and some of the resins were extensively used as fixatives, but most of these substances either had such a powerful odor, color, or sticky qualities (resins), that they could not always be used in sufficient proportion to entirely satisfy. Here modern organic chemistry has given us a number of substances, which, while practically of no odor value themselves, are very valuable in combination, because they not only serve as fixatives,—that is, make odors with which they are mixed less volatile, but in many instances have the tendency to sweeten the odor. Among representative instances of this class we may mention methyl anisate, benzyl benzoate, benzyl cinnamate, and benzyl-iso-eugenol, which have but little odor. Synthetic ambergris and civet, while strongly odoriferous, are usually not employed for their odor value, but because they act as fixatives. Then we have a group of very useful materials which combine a delightful odor with valuable fixative properties, as the many varieties of artificial musk, phenylethyl phenylacetate, which has a charming rose-like fragrance, the various moss odors as Mousse de Chene, Mousse de Perse, Mousse d'Orient, and many other products valuable as fixatives wherever their odor harmonizes with the other constituents utilized.

Chemical Groups of Most Importance. If we briefly review the chemical groups of substances which are of most value to the industry, we may mention aldehydes, ketones, phenols, phenolic ethers, alcohols and esters. Esters especially—that is, combinations of alcohols with acids, are frequently of great value as constituents of some of the best-known odors and flavors. The acids alone are usually of but little importance. In ester form, however, when combined with the various alcohols, they are among the most useful constituents known. This brings us to

one aspect of the case, which is of special importance to the chemist who studies for industrial purposes.

Industrial Application. In a great many instances the user of a perfume or flavoring material does not consider the chemical changes or influences against which it may have to contend. All esters are sensitive to alkalies, and yet the writer has seen innumerable instances, when, thoughtlessly, perfume materials or flavoring materials that owe their entire value to esters have been used in combination with alkalies, which will saponify the ester in a very short time, and the odor will of course disappear. This illustrates the importance of having the student become acquainted with the individual constituents of either odors or flavors, so that he may use them intelligently and will not employ a product that will decompose under the influences with which it may have to contend and so that the odor or flavor may endure. This will also show that care is necessary in selecting an individual material for a certain purpose, to be sure that it will answer and that it will not be destroyed. When we remember that either odoriferous or flavoring materials are used in small proportion only, we realize all the more that chemical incompatibility must be avoided by all means, if we wish to produce an article that will give satisfaction.

Of the crude perfume materials used by the ancients, but few are used at the present time. The animal secretions of value to the industry are very few, namely, musk, civet, ambergris, and allied odors.

Musk. Musk is perhaps one of the oldest perfume materials in existence and consists of the dried secretion of the preputial follicles of the male musk deer. This animal has been hunted so excessively that it has become practically extinct and it is now found only in the portion of Asia where the Himalaya Mountains rise to elevations of 8000 to 12,000 ft. Occasionally the animal may wander into lower altitudes, but the greater part of the annual production comes from the Himalaya region. In Siberia we find musk deer, allied in family, but the musk secreted by them is not valued as highly in commerce and does not have as powerful an odor. The musk pods are purchased by native dealers, carried by caravans to the seashore and marketed from Chinese seaports. Commercially the product is known as either Nepaul or Tonquin musk and is now valued at from $20 to $25 an ounce. It is becoming scarcer each year, and the time is not far distant when the musk deer will be extinct, because each musk pod means that a male musk deer has been killed. Of course adulterations are plentiful. The Chinese have excelled in this, and have for many years past sold so-called artificial musk, which is a mixture of dried blood and various other substances, hard to identify, with just a trace of natural musk, marketed at prices ranging from $1 per ounce, upwards. The chemical substance to which musk owes its odor has never been definitely identified. Some research work of recent years seems to point to a ketone, which gives a powerful musk odor, but no chemical work of note has been done

on the subject, owing to the high expense involved, and the exact chemical formula of the product is still in doubt. Musk also contains a number of impurities, which rather detract from the true musk odor, but are always present in the natural article.

Synthetic Musk. If we now turn to synthetic musk, we find that here we encounter a product differing entirely in chemical composition, imparting a musk odor, and of which many chemical derivatives have been made. The original musk marketed was a trinitro derivative of toluene, and later a trinitro derivative of xylene. This brings us again to the parent substance of so many valuable materials in chemistry and medicine, namely, coal tar. Xylene, which forms a considerable proportion of coal tar, may be condensed with iso-butyl chloride, by means of aluminium chloride, —that is by the well-known Friedel and Kraft reaction, to form iso-butyl-xylene. After careful purification, this substance is nitrated in the usual way, by employing a mixture of sulphuric and nitric acids, and the final product is thoroughly purified by repeated crystallization. This gives us the artificial musk of commerce, trinitro-iso-butyl-xylene, $C_{12}H_{15}O_6N_3$, consisting of small, yellowish, needle-shaped crystals, having a peculiar musk odor. This artificial musk is utilized in many perfume compositions all over the world to-day, and while it has not the identical odor of natural musk it has replaced it in numerous instances in the soap and perfume industry. The success of these products encouraged scientific research, and as a result a number of other musk compounds have been made which have a stronger and sweeter odor. Among these we may mention musk ketone, also a nitro product, in which, however, the CO or ketone group is present. Ambrette musk, and similar derivatives, made by other complicated chemical processes have a more intense odor than any other artificial musk known and some of them have the advantage of being more soluble.

Civet. Civet is the secretion of the civet cat of Abyssinia, where the cat is kept for the purpose of producing a regular supply. It is a substance somewhat similar to musk, but contains derivatives of indol, principally one of the methyl-indols, as active constituents. As brought into commerce, it is largely adulterated with fats and fatty substances, hairs, clay, etc. The substances present in natural civet, which give it fixative value, have been identified chemically and are produced synthetically. Civet materials are now available, both in liquid and crystal form, as well as the active principle to which the odor of civet is mainly due, namely, one of the methyl indols, C_9H_9N.

Ambergris. Ambergris is another product belonging to this series, and is supposed to be a decomposition product present in the intestines of unhealthy whales. Its use has largely decreased in recent times, as synthetic substitutes have become available at a small fraction of the cost of the natural article, the supply of which is very irregular and uncertain.

Castoreum. Castoreum is a product from the beaver, which has a similar odor to musk. It is now but seldom used.

Gum Benzoin. Of the fragrant gum resins known to the ancients, but few have survived. Gum benzoin is used in medicine to-day and forms a constituent of many toilet preparations. Sumatra gum benzoin has a dark brown color and is only fit for medicinal use,—it should never be employed for perfumery purposes. The gum coming from Siam or Rangoon is the only variety suited for use in perfumery. It is practically colorless. Gum benzoin is chemically of interest, because from it benzoic acid was first isolated and it has given its name to the chemical benzene or benzol C_6H_6. Then we have gum olibanum or frankincense, and myrrh—Arabian gums of sentimental, rather than practical, importance, although used in the manufacture of incense.

Styrax. Styrax from Asia Minor is another gum of decreasing importance, in which, however, important chemical bodies have been found,—among them styrol previously mentioned, as well as cinnamic acid and cinnamic alcohol, both of which are of importance.

Balsam Peru. Balsam or gum Peru, is improperly named, because all of it comes from the Republic of Salvador in Central America. This balsam is obtained by crude methods over a direct fire and has a rather smoky odor. It is too sticky to find application in perfumery and is employed in medicine. There is, however, the so-called oil of balsam Peru, which is separated from the balsam by chemical means, eliminating the resins, which has a very nice odor, although contaminated by the burned smoky smell, due to the phenolic constituents, which result from heating the balsam over direct fire. The product has been analyzed repeatedly and synthetic reproductions are on the market, which are superior in odor to the natural.

Gum Labdanum. Then we have the old gum labdanum, mentioned in some of the ancient works on perfumery, the black color and stickiness of which prevented its extended use. Chemistry has enabled us to isolate from the gum the portion to which the real odor is due, which is now largely employed in the most modern creations and imparts all of the odor value and fixative value of the gum, without the color and stickiness. Labdanol is indispensable in many high-grade bouquets, as it imparts a delicate softness to the odor and acts as a most excellent fixative as well.

Flower Perfume Materials. These include our finest odors, perfumery products isolated from the flowers by means of either the enfleurage or maceration process, or synthetic reproductions of these materials. All of these products are exceedingly complex in character and owe their fine perfume to the proper blending of many distinct chemical bodies, produced in such lavish profusion in nature's laboratory. These materials form the most important group available for duplicating the delightful blossom fragrance, and include all blossom oils, concretes, " absolutes," pomades, and washings from same, and all the fine synthetic

flower perfume oils. Many of the different flower odors contain a number of the same constituents, but in widely differing proportions and influenced by the odor of other bodies present.

Geraniol and Citronellol. In the rose we find the terpene alcohols, geraniol and citronellol, present in large proportion. These are closely allied chemically. Geraniol has the formula $C_{10}H_{18}O$, and citronellol $C_{10}H_{20}O$. Geraniol may be produced more economically from a number of the cheaper oils, as will be shown later. Citronellol has not been found alone, but is usually accompanied by geraniol. As the commercial separation of these two alcohols is only possible by destroying the greater part of the geraniol present, the use of citronellol alone, which does not exist by itself in the flower anyway, is not advantageous. Under the name of rodinol, or rhodinol, a mixture of geraniol, citronellol, and isomeric alcohols is marketed, containing the proportion of allied alcohols present in roses. It has a very sweet rose-like odor when perfectly pure and is used in quantities. Citronellol is also produced artificially from the allied aldehyde, but this product lacks that soft sweetness which is the characteristic of rodinol. The esters of geraniol and rodinol are likewise of importance, the acetates, formates, and propionates having a very sweet flowery odor.

Rose Oil and Rose-flower Products. We have already mentioned the history of oil of rose, usually known as Turkish otto, one of the highly-prized perfumery products used throughout the world. Turkey does not produce even a small proportion of the crop; almost all of it comes from Bulgaria; of late Asia Minor and Persia also produce a limited quantity. Yet it must be remembered and repeated that distilled oil of rose has only part of the perfume of the flower. The very act of steam-distillation destroys some of the most valuable constituents present in the petals. As previously mentioned the oil consists largely of geraniol, citronellol, and allied alcohols with a small proportion of their esters, as well as about 20 per cent of an entirely odorless, waxy hydrocarbon belonging to the paraffine series. Much of the oil is impure. The official figures show the importation into Bulgaria of quantities of products that may be used as adulterants for oil of rose and the export of a great deal more rose oil than the statistics show has been produced. The rose-flower products have a much finer perfume than the distilled oil, or otto, and are available in many modifications. Rosa centifolia is used for manufacturing rose concretes, pomades, and absolutes. The blossom oil contains up to 80 per cent of alcohols, principally phenylethyl alcohol (see below), which is almost entirely absent in the steam-distilled otto, as it passes into the rose water Oils imparting the odor of the tea rose, red rose, moss rose, white rose, and other varieties, are available. All of these members of the rose family contain other constituents in varying proportions, hence in order to duplicate their odor we must utilize many different chemical bodies.

Patchouly Oil. Oil of patchouly is an illustration. When added to rose products in infinitesimal proportion it helps to duplicate the peculiar odor of the white rose. The patchouly plant is principally obtained from the Straits Settlements and Java, where it has been cultivated so long that it has almost wholly lost the habit of flowering. The oil, which is distilled from the leaves, increases in value on aging. By chemical methods the oil may be purified and the undesirable constituents which have a moldy, disagreeable odor, removed. The resulting products can be used without hesitation in the finest perfume combinations, but only in small proportion. If employed in too large a quantity the effect will not be agreeable.

Phenylethyl Alcohol and its Derivatives. Phenylethyl alcohol, $C_6H_5CH_2CH_2OH$, and some of its derivatives are present in roses and many other flowers. The alcohol itself has a faint flowery odor. It forms nearly 60 per cent of the rose extract blossom oil. Some of its esters are very valuable, the acetate and formate having a decidedly fruity character which imparts freshness to blossom oils containing these esters. The benzoate gives a very pleasant odor and also acts as a fixative. Phenylethyl phenylacetate has a very sweet odor, reminding one of roses and hyacinths, and owing to its high boiling-point is a very valuable fixative. Phenylethyl propionate also has a fruity character, yet is very flowery when used in traces.

Phenylacetic Acid Esters. The allied phenylacetic acid has a disagreeable odor (compared by many to a stable odor), but some of its esters are valuable, both as perfumes and flavors. The ethyl, methyl, amyl, benzyl and phenylethyl esters are mostly used. The ethyl and methyl esters give a very sweet, honey-like fragrance when used in minute proportion. The amyl and benzyl esters have a very flowery character. We find the phenylethyl or phenylacetic group very widely distributed in many different blossoms, only different derivatives and different proportions are present in each flower.

Phenylacetic Aldehyde and Hyacinth Oils. The allied phenylacetic aldehyde, $C_6H_5CH_2CHO$, is a thin, limpid liquid when freshly distilled, becoming syrupy very quickly, and has a very strong and pungent hyacinth odor; it is usually marketed as jacinthe. Unfortunately it is very unstable and changes quickly into polymers on standing. Hence, a solution in benzyl benzoate or some similar solvent is to be preferred. Commercial brands often contain the cheaper benzaldehyde. Brom styrene $C_6H_5CH{:}CHBr$, also has a strong hyacinth-like odor. Hyacinth blossom oil contains also a number of other constituents.

Hydratropic Aldehyde. The instability of phenylacetic aldehyde, which has such a sweet odor, prompted research work to find some derivative which would have a similar odor but would keep unchanged. Among the many derivatives made, phenylmethylacetic aldehyde, $C_6H_5CH.CH_3.CHO$, or hydratropic aldehyde, was found to be perfectly

stable. This differs from phenylacetic aldehyde only in so far as one hydrogen is replaced by the methyl group. It has a very fine and pungent flower odor, which, however, is much stronger than phenylacetic aldehyde. By condensing benzene with any halogen derivative of isopropyl-alcohol, replacing the OH of the alcohol by a halogen by the usual method, iso-propyl-benzene is obtained. After properly purifying the resulting product, we obtain hydratropic aldehyde by oxidation. A number of its derivatives are likewise of importance. For instance, the methyl derivative, readily obtained by using toluene instead of benzene in the above process, has an even stronger and more pungent odor,—in fact, it is so powerful that the odor is disagreeable when concentrated, but minute traces of it produce very pleasing results in blossom oils.

Cinnamyl Alcohol and Cinnamic Acid Esters. While speaking of materials that have a hyacinth-like odor, we must not overlook cinnamic alcohol, $C_6H_5CH{:}CHCH_2OH$, which imparts a very sweet and flowery, though mild, perfume. This alcohol is one of the constituents of gum storax, and is present in it as such, as well as in ester form in combination with cinnamic acid, $C_6H_5CH{:}CHCOOH$, as cinnamyl cinnamate, a practically odorless white solid, and also in combination chemically with some of the acid resins of the gum. While cinnamic acid has practically no odor value, its esters are of value, as they give a fruity effect when used in small proportion and they are present in many flower oils. The methyl, ethyl, and amyl esters are the most valuable from the odor standpoint, the first two also being used in the flavoring industry. When used in traces they assist in duplicating some of the fine fruit flavors of nature. The benzyl ester, benzyl cinnamate, we have already mentioned as a good fixative, although it has very little odor. Phenylpropyl alcohol or hydro cinnamic alcohol, $C_6H_5CH_2CH_2CH_2OH$, and some of its esters, are also present in some flower oils.

Benzyl Alcohol and its Esters. In many of the perfume flowers we find either benzyl alcohol, $C_6H_5CH_2OH$, or its esters, which are most widely distributed throughout nature. Benzyl acetate, accompanied by the formate and propionate, is an invaluable constituent in jasmine, of which indeed these esters form the bulk. The same compounds may also be found in tuberose, ylang ylang, and many other of the finest blossom oils. Benzyl alcohol is easily prepared. By chlorinating toluene we form benzyl chloride, and by exchanging the chlorine for either the hydroxyl group or for one of the acid radicals, we may obtain at will either the alcohol or any of its esters. Any of these esters may also be made from the alcohol, and some of them are so prepared by condensation in the usual way. Benzyl acetate has a very fruity odor, and has found favor itself as a soap perfume, in combination with other materials. Alone it is too fleeting, and has a somewhat pungent and harsh odor. Commercial brands are often very impure. Benzyl formate and benzyl propionate give a totally different odor effect from the acetate. It there-

fore can readily be seen why flowers that contain a mixture of the three esters will have an entirely different odor from either one alone. On the other hand, benzyl benzoate, the benzoic acid ester of benzyl alcohol, has only a slight odor, but is a normal constituent of many natural blossom oils and is highly valued as a solvent and fixative. It is extensively used for dissolving artificial musk crystals. While it requires about 12 to 14 pints of spirit to dissolve an ounce of artificial musk, this amount is freely soluble in 4 ounces of benzyl benzoate on warming, and may then be mixed with other oils in any desired proportion. Benzyl benzoate also has been used to some extent as a fixative in flavors, as it makes the more volatile flavors permanent, especially in cases where the flavor has to stand prolonged heating, as in the confectionery industry, in making chewing-gum, and for other commercial applications.

Benzoic Acid Esters and Allied Derivatives. While the benzyl ester of benzoic acid has little odor, the methyl, ethyl, isobutyl, and amyl esters of benzoic acid, C_6H_5COOH, have powerful odors. The methyl ester is used extensively in the soap industry under the name Oil of Niobe. The ethyl ester is used more often as a flavor, and when properly employed imparts characteristic freshness to many fine fruit oils. Some of the derivatives of benzoic acid are very important. For instance, ortho-amido-benzoic acid, $C_6H_4(NH_2)COOH$, which has the same formula as benzoic acid, excepting that one hydrogen in the ortho position to the carboxyl group is replaced by NH_2, is the parent substance for both methyl anthranilate and dimethyl anthranilate. Methyl anthranilate is the methyl ester of ortho-amido-benzoic acid or anthranilic acid. It is responsible to a great extent for the delightful odor of the orange blossom, and clearly shows the inferiority of the steam-distilled neroli oil, compared with the orange-flower products made by enfleurage or by synthesis. Commercial products often contain aniline and other bases; only the perfectly pure ester has a fine flower odor. It forms white crystals, melting at 24° C. Its solutions, even when very dilute, are highly fluorescent. The distilled oil usually contains less than 1 per cent of this ester while the flower product proper contains up to 15 per cent. Even in great dilution its odor value is considerable, and it is more widely distributed than has been commonly recognized; traces of it have been found in many blossoms, while jasmine, tuberose, ylang ylang, and other fine flower oils contain appreciable amounts.

If we substitute a methyl group in amido benzoic acid, we obtain methyl-amido-benzoic acid and the methyl ester of this, or dimethyl anthranilate is likewise very valuable. It has a sweet odor in great dilution, which imparts fragrance to many blossom oils.

Linalool. Linalool is a terpene alcohol of high importance in the industry. It has the chemical formula $C_{10}H_{18}O$, and is widely distributed in nature. Mexican oil of linaloe is the principal commercial source of linalool, as this oil contains from 60 to 85 per cent. The oil itself

has a crude odor, owing to impurities, but by proper physical and chemical methods the alcohol may be separated in very pure form. The so-called oil of female rosewood distilled in British and French Guiana contains a larger proportion of linalool and has a sweeter odor itself, but the terpene alcohol separated from it, when properly purified, is in no way superior to the Mexican product, provided care has been taken to eliminate all impurities. Linalool also exists in several isomeric modifications differing somewhat in odor. Oil of coriander contains about 65 per cent.

Lily-flower Oils. These contain linalool, its derivatives and esters, also products belonging to the ionone series, which will be discussed later, phenolic ethers, and some of the higher aldehydes and alcohols of the fatty series, which we shall speak of further on.

Orange-flower and Neroli Products. One of the oils which owes much of its odor value to esters of linalool is the oil of neroli, distilled from orange blossoms. We have already mentioned methyl anthranilate and a number of other substances that contribute to the complex orange-flower odor. Neroli oil, being made by steam distillation, does not represent the entire odor value of the flowers, but having become a commercial product many years ago, is esteemed by manufacturers of cologne, and is also used as a flavor to a limited extent. "Orange-flower water" is obtained as a by-product, and contains the saponified portion of some of the constituents present in the blossom. It may be had at a fair price, considering the fact that the purchaser must pay for the transportation of distilled water from Europe. A number of different varieties of neroli are known, neroli petale being the finest grade, neroli bigarade coming next in quality, after which there are various inferior grades, ending with the so-called oil of petitgrain. This is imported from South America, where it is distilled by crude native methods from twigs, leaves, unripe fruit, as well as flowers of the wild orange trees, which have spread from those planted there when Spanish friars controlled that quarter of the world. Oil of petitgrain is frequently used to dilute the more valuable neroli oils. Orange-flower products made by enfleurage or synthesis differ greatly in composition from distilled neroli oils as they represent all the blossom constituents. As previously mentioned they contain a much larger percentage of methyl anthranilate, also phenylethyl alcohol and its derivatives and other constituents which are lost in the steam-distillation process. The flower oils therefore have a much sweeter and finer perfume than neroli oils and are indispensable in fine perfumery.

Jasmine-flower Products. These should be discussed here, as they contain many of the items just mentioned. The jasmine odor is one of the most useful perfumery raw materials, indispensable in many bouquets, as it imparts great freshness and delightful odor effects. Jasmine-blossom oil contains principally the benzyl esters of acetic, formic, and propionic acids, linalool and its esters, methyl anthranilate, benzyl alcohol, geraniol,

para cresol, a ketone jasmon and traces of a number of other constituents. Cape jasmine or gardenia oil belongs to the same odor class, but is less fleeting and has a more intense sweetness.

Tuberose, Jonquil, Narcisse Products. These again illustrate the fact that nature's finest blossom oils often represent some of the same constituents, as these oils contain many of the items present in orange-flower, lily and jasmine oils—but in different proportion, and the odor is modified in each case by other bodies.

Naphthol Ethers. It is curious to note that organic chemistry has also produced an ether of a phenol, a direct derivative of naphthalene, which has an odor somewhat similar to orange flower, and it is so powerful that the material can only be used in minimal amounts. While the odor is not equal to the flower, it is cheap and so strong that quantities of this ether are used in soap-making and in the cheaper grades of cologne. This is the ethyl ether of beta-naphthol, which may readily be derived from naphthalene. Beta-naphthol condenses very easily with ethyl alcohol and the resulting white or yellowish white crystals, melting at 37° C., are known as bromelia or neroline, $C_{10}H_7.O.C_2H_5$. The latter name, however, has been indiscriminately applied both to the ethyl and methyl ether of beta-naphthol. The methyl ether is known as yara, has an even more powerful odor, but reminds one somewhat of acacia blossoms rather than orange flowers and has a higher melting-point,—that is, 70° C. Its odor is disagreeable to many people, owing to its excessive strength and because it is often employed in far too large proportions. In soaps both these ethers may be used in the proportion of from $\frac{1}{4}$ to $\frac{1}{2}$ ounce to 100 pounds, always in combination with other perfume materials. Neither of these ethers has been found in nature, and this is an instance where products totally differing in chemical composition have a similar odor, as in the case of natural and artificial musk, which are not related chemically.

Phenol Ethers and Allied Bodies. Another illustration that carbon compounds having a totally different structure may resemble each other in odor is supplied by di-phenyl oxide $\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\!\!>\!O$. This ether of phenol has a very powerful odor somewhat similar to geranium. As it is made from phenol by condensing two molecules with the loss of H_2O, or by replacing the hydrogen in the hydroxyl group of phenol with the benzene ring, it often has a carbolic by-odor due to insufficient purification. Only the chemically pure ether, free from all traces of by-odor, should be employed. Another body which recalls the odor of geranium is diphenyl methane $\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\!\!>\!CH_2$. It can be readily made from benyzl chloride by replacing the chlorine with the benzene ring. When absolutely pure it has a very strong and quite sweet odor. Para-cresol or

para methyl phenol $C_6H_4(CH_3)OH$ has been found in traces in several of the fine blossom oils and its methyl ether, methyl para-cresol $C_6H_4(CH_3)O.CH_3$ is the body to which oil of ylang, one of our sweetest flower oils, owes its characteristic odor.

Ylang Ylang Oil. Ylang ylang oil has long been one of the most valuable products of the Philippines. The distilled oil is a very complex body which differs somewhat from year to year and according to the method of production. In fact, ylang and cananga, a cheaper oil, are derived from the same tree. The best ylang ylang oil consists of the first portion of the steam distillate. It contains a larger proportion of esters. Cananga oil represents the less valuable fractions, forming the second portion of the distillate. Its odor is not nearly as sweet and its value is often less than 10 per cent of ylang oil. Many of the chemical bodies that we have described are present in this oil, therefore it is a fine example of a complex natural product. It contains benzyl alcohol, benzyl acetate, benzyl formate, benzyl benzoate, benzyl salicylate, methyl anthranilate, methyl benzoate, methyl salicylate, geraniol, geraniol acetate, linalool, linalyl acetate, eugenol, iso-eugenol, methyl eugenol, methyl iso-eugenol. This list, while long, is by no means complete, as a number of allied bodies, especially other esters, are also present. Even all these together will not give the right odor, until the characteristic constituent is added which converts the product into ylang ylang. This body is the methyl ether of para-cresol, which is enormously powerful and therefore must be used with great care. Traces of para-cresol itself and of guaiacol ethers are also present in the oil.

Acetophenone and its Derivatives. Among aromatic substances having a flowery odor, we must not overlook phenylmethyl ketone $C_6H_5.CO.CH_3$ known also under the name of acetophenone and hypnone, the last name being due to the fact that some years ago it was used in medicine as a hypnotic. It is a product particularly valuable in soaps, as it is stable against alkalies under all circumstances. Its delightful flower-like odor and pungency make it a valuable addition in combinations where proprietary effects are desired. A close chemical relative of this substance is para-methyl-acetophenone, having the same formula but with an additional CH_3 group in the para position to the ketone group CO, $(C_6H_4(CH_3).CO.CH_3)$. In commerce this is usually called melilot, although many fancy names have been used. It imparts the honey-like fragrance of sweet clover and gives very similar effects to cumarine, the active principle of the tonka bean. As it is about five times as powerful in odor as cumarine it is one of the most economical perfumery substances known. In soaps it is invaluable as it is likewise absolutely stable against alkalies. Methyl melilot or di-methyl acetophenone $C_6H_3(CH_3)_2COCH_3$ recalls the odor of melilot, but is still sweeter and much finer in character. Other more complicated chemical derivatives of these substances are also used.

Cumarine. Cumarine $C_6H_4(O)CHCHCO$ is the active principle of tonka beans and is also widely distributed in nature. It is found in quantities in the herb known as deer tongue and in small proportions is present in hay. The odor of new-mown hay in the fields is due partially to this substance. From the chemical standpoint, cumarine is interesting, because it can be made from carbolic acid or phenol, which in turn brings us back again to coal tar, which has furnished so many surprises to chemists. Phenol, by treatment with alkalies and chloroform may be readily converted into a mixture of two aldehydes. We mentioned these as an illustration in speaking of the futility of judging the value of a compound by its chemical formula. Ortho-oxy-benzaldehyde is usually formed in the larger proportion and may be readily converted into cumarine by the well-known Perkin reaction, by condensing this aldehyde with acetic anhydride and anhydrous sodium acetate. After proper purification, the chemical so prepared cannot be distinguished from a properly purified cumarine obtained either from deer tongue or from the tonka bean. Purification is of prime importance because the slightest odor of the parent material, or of one of the reagents, adhering to the finished product will entirely spoil it. Cumarine is largely used in making cheap flavors, also in perfumery and in scenting soaps. Some of its chemical derivatives, the manufacture of which is more complicated, are even more valuable.

Hawthorn, Aubepine, New-mown Hay Oils. Para-oxy-benzaldehyde is the other aldehyde formed in smaller proportion in the reaction just mentioned. While a nearly odorless solid it can readily be transformed into the methyl derivative, an oil of powerful odor, recalling hawthorn blossoms and known as aubepine, $C_6H_4(OCH_3)CHO$. New-mown hay perfume oils contain several derivatives of the constituents just discussed and should be mentioned here as they are so valuable as sweeteners in many perfume formulas.

Salicylic Acid Esters. We have just considered melilot as imparting a sweet clover fragrance. The red clover has an odor of its own. One of the main constituents used in duplicating this is a synthetic body, first made in the laboratory and long marketed under various names, as orchidee, sanfoin, etc. This is the iso-amyl ester of salicylic acid or ortho-oxy-benzoic acid $C_6H_4(OH)COOC_5H_{11}$. It has about the same relation to trefle or orchid perfumes as benzyl acetate has to jasmine,—that is, while present in large proportion, its odor is influenced and totally changed by some of the other constituents previously described. Iso-butyl-salicylate has a similar odor and is known under the name of orchidone. Trefle-flower oils are built by synthesis from these and other esters in much the same way as jasmine oils are produced with the help of benzyl acetate or rose oils with the assistance of the terpene alcohols. Trefle odors have become very popular and are also used extensively in toilet soaps.

Birch Oil. Birch oil is almost entirely composed of the methyl ester of ortho-oxy-benzoic acid or salicylic acid. This is also the main constituent of value in oil of wintergreen. For this reason the U. S. Pharmacopœia has recognized artificial methyl salicylate, made by condensing salicylic acid and methyl or wood-alcohol. For flavoring, methyl salicylate is much inferior to ethyl salicylate, which also exists in many natural oils, as the ethyl ester gives not only a sweeter, but more lasting flavor.

Wintergreen Oil. Oil of wintergreen represents one of the exceptions among essential oils as it consists of practically one constituent to which the odor and flavor value is due. Almost all others are much more complex in character. Methyl salicylate, mixed with a little ethyl salicylate, and a trace of the methyl ester of methyl salicylic acid, can scarcely be distinguished in flavor from the natural oil. It is not surprising therefore that these natural oils are so largely adulterated, for while the synthetic oils are legitimate articles of commerce, they should not be supplied where the natural product is ordered, as this is much higher in value, due to cost of production.

Camphor and Safrol. Camphor $C_{10}H_{16}O$ is a body, which, while not an essential oil, is very important, not only on account of its medicinal value, but because it is the parent substance of many other chemical bodies. Japan has controlled its production, but it has also been made by synthesis and artificial camphor is now on the market. Camphor is obtained commercially by distilling with steam the wood of the camphor tree. Recently, the discovery has been made by the U. S. Department of Agriculture Experiment Stations, that small plants, just started from the seed, can be mown and distilled with a very good yield of camphor. Camphor is a solid which crystallizes from camphor oil on chilling. The crude product is imported from Japan and refined in the United States. Camphor oil, the liquid portion, is very complex, and is one of the sources of safrol, which is used commercially in medicine as artificial oil of sassafras, of which this is the principal constituent.

Sassafras Oil. As stated above safrol $C_{10}H_{10}O_2$ is the main constituent of this oil, of which it forms 80 per cent, the balance consisting of 7 per cent camphor and terpenes. It finds employment in medicine and for scenting laundry soaps.

Heliotropine and Heliotrope-flower Oils. Safrol is also used chemically. By oxidation it yields heliotropine or piperonylic aldehyde, $C_6H_3(OCH_2O)CHO$, the methylene derivative of protocatechuic aldehyde. This substance has the odor of heliotrope and is one of the constituents to which the flower oil owes its perfume. Alone, however, it lacks strength and character and must be reinforced with other bodies present in the blossom. Heliotropine crystals have proven valuable as an addition for sweetening soap perfumes and for other technical applications. Heliotrope-blossom oils are among the most useful

products available for perfumery, as they are much used for sweetening many other flower odors.

Bitter Almond Oil and Benzaldehyde. The essential oil of bitter almond is an illustration of the futility of the classification of essential oils according to their botanical origin. The almond tree is a member of the great rose family, resembling our peach. There is no difference between the bitter and the sweet almond trees, and the fruits of both contain a considerable amount of fatty oil, which is also utilized in medicine as "oil of sweet almonds." A similar oil may be found in the apricot and peach fruit, but in addition, these two and the bitter almond kernel contain a body called "amygdalin," which is a combination of glucose, hydrocyanic acid and benzoic aldehyde, and this breaks down into these bodies when acted upon by a ferment, called emulsin, which is also present in the fruit or seed, or by other hydrolizing agents. After the emulsin has acted, direct steam is applied, and a very old process in vogue among the alchemists, and named by them "cohobation," is employed. The water which has been distilled off is returned to the still after separating the oil, by which means the total amount of water used is kept down to a minimum and a much larger quantity of oil is recovered. The hydrocyanic acid must be removed from oils intended for flavoring, because it is highly poisonous, and during this and the previous handling care must be taken to prevent, as far as possible, the rapid oxidation of the principal constituent, benzaldehyde, to benzoic acid. This will well illustrate the care which must be taken, and the number of reactions involved, in obtaining from nature such a simple body as benzaldehyde, which can be so easily made from toluene. For instance, if toluene is treated by chlorine, we obtain according to the proportion of chlorine employed, either benzyl chloride $C_6H_5CH_2Cl$ or benzal chloride $C_6H_5CH.Cl_2$. Benzaldehyde may be made from either of these toluene substitution products. For instance, if we treat benzyl chloride with lead nitrate and water, we obtain benzaldehyde C_6H_5CHO. The oil of bitter almond, deprived of prussic acid, is commercially known as oil of bitter almond, S. P. A. (without prussic acid). The natural oil containing the acid is very poisonous and must never be employed, excepting for medicinal purposes when the prescribing physician specially desires its medicinal effects.

Benzylidineacetone. This condensation product of benzaldehyde and acetone, benzylidineacetone $C_6H_5CHCH.CO.CH_3$, or cinnamyl methyl ketone, has a very powerful odor, reminding of cumarine, hence it has been marketed as cumarol and under similar fancy names. It is stable against alkalies and is used as a soap perfume. But it is exceedingly irritating to the skin, and should therefore be used in only very small proportion and never as a constituent of perfumes employed in creams, or toilet lotions.

Anise Oil. Anise oil is easily obtained, as it is only necessary to steam-distill the seed until the residue is free enough from oil to be used as

cattle food. The resulting anise oil is quite complex in composition, the main constituent being anethol $C_{10}H_{12}O$, the methyl ether of para-propenyl-phenol, and with it is associated the corresponding allyl compound known as iso-anethol, methyl chavicol, or estragol $C_{10}H_{12}O$. These bodies are also found in almost the same proportion in an entirely different oil from a botanical standpoint, because anise is a member of the Umbelliferous family, to which carrots and parsnips belong, while the star anise is distilled in China from the fruit of an ilex tree, which is related to magnolia, and yields an oil which can scarcely be distinguished by chemical test from true anise oil. Star anise oil is usually produced in the crudest ways by natives and is sold at a much lower price. The oil is used in medicine and sometimes as a flavor.

Bay Oil. Bay oil is in no way related to the bays or laurels of classical times, but is distilled from leaves of trees native to the West Indies, belonging to the Pimenta or Myrcia family. At an early date these sweet leaves were soaked in rum, and the well-known bay-rum was the result. It was later found that an oil obtained by steam distillation could be added to alcohol, and a very similar product obtained. The oil contains eugenol and methyl eugenol as its principal constituents. It also contains chavicol $C_6H_4(OH)C_3H_5$, and its methyl ether, which has been mentioned previously as present in anise oil, and a little citral, which we shall consider later. In addition there are a number of terpenes, which are bodies that have only recently been investigated and about which we shall have to learn much before we can understand them. They are present in many oils in considerable proportion and in traces in nearly all essential oils that are distilled. They are a disadvantage in practically every instance, as they take up oxygen from the air, thicken the oils, give rise to unpleasant odors and have but little odor value themselves. Many of the natural oils contain a large proportion of terpenes, and therefore a purified product which eliminates these is highly to be preferred in manufacturing, because the purified oil is more soluble, has the odor of the plant or fruit in a higher degree, and is more concentrated.

Citrus Oils. The oils of the Citrus family, which include bergamot, lemon, lime, orange and bitter orange are made commercially principally in southern Italy and Sicily. (Oil of orange is also made in Jamaica.) All are obtained by expression and not by distillation.

Bergamot Oil. Oil of bergamot owes its odor principally to the esters present, consisting of linalyl acetate and allied compounds. The commercial oil usually contains from 30 to 40 per cent of ester and is valued according to ester content. It has been largely adulterated, especially since the price has risen during the last few years, and should be purchased from reliable sources. Synthetic products are available, which duplicate the odor at considerably less cost.

Linalyl Acetate. This is one of the most important perfume esters. It is prepared extensively by synthesis from linalool. As it forms

the main odoriferous constituent of oil of bergamot, linalyl acetate, $C_{12}H_{20}O_2$, replaces this to advantage, owing to its lower cost, as one pound of 80 per cent ester is equivalent to over 2 pounds of bergamot oil. Much of the commercial linalyl acetate is impure and often contains other esters, principally impure terpineol acetate. When pure it has a very fragrant odor. It is present in many blossom oils, which indicates its usefulness. It forms part of the odor value of the oils of orange flowers, jasmine, gardenia, ylang ylang, lavender, etc.

Lemon Oil. Lemon oil consists principally (over 90 per cent) of terpenes, which have no flavor or odor value, but which hasten the rapid oxidation of the oil, so that lemon oil will not keep very long and changes into turpentine-like-smelling derivatives, which are useless for technical application. The active principles of lemon oil consist of about 8 per cent, the main constituent being citral, the aldehyde of geraniol, which we shall further consider under geranium oil. Citral is usually isolated from lemongrass oil, in which it is present in far larger proportion, ranging from 60 to 80 per cent, according to quality. Lemongrass oil contains, however, other constituents that have a disagreeable odor. Citral alone, even when pure, does not produce a fresh lemon flavor. It is well known that other substances are present in small proportion, for instance, small amounts of linalyl acetate, methyl anthranilate, and a number of other compounds. Lemon oil is used mainly as a flavor. Where a lemon *perfume* is wanted, as in soaps, citral may be used to much better advantage at a large saving in cost.

Orange Oil. The oils of bitter and mandarin oranges and limes are made on a small scale, but the oil of sweet orange has found extended application in flavors and perfumery for many years past. Oil of sweet orange contains a larger proportion of terpenes, which are useless from the odor and flavor standpoint, than any of the other oils of the Citrus family. In fact, it is estimated that less than one-twentieth of the weight of the commercial oil of orange consists of the active odor or flavor-bearing portion—among these decoic aldehyde has been identified as one of the constituents that contributes the main flavor, but many other items are present.

Synthetic Aldehydes and Alcohols. This brings us to the subject of the synthetic fatty aldehydes and alcohols, which are of use in perfumery and flavors. The lower fatty aldehydes and alcohols, containing less than seven carbon atoms to the molecule, are not useful constituents, the C_3, C_4, C_5 and C_6 aldehydes having a very disagreeable odor. Our interest begins with heptoic aldehyde $C_7H_{14}O$ and heptoic alcohol $C_7H_{16}O$. Both of these may be made from castor oil commercially and have an exceedingly disagreeable odor while impure, but the pure products when used in traces often prove of high value. Then we come to the eight-carbon atom molecule, octoic alcohol $C_8H_{18}O$ and octoic aldehyde, $C_8H_{16}O$, both of considerable importance in perfumery. They

are present in many of our most valued flower oils, but in infinitesimal proportion. Yet if both of these are utilized indiscriminately in larger quantities the result will be failure, because while concentrated both have a disagreeable odor. Almost the same thing may be said of nonoic aldehyde $C_9H_{18}O$ and nonoic alcohol $C_9H_{20}O$, both of which are extremely valuable when used in traces, yet when employed in too large a proportion the odor effect is entirely out of harmony and spoils the product. Decoic aldehyde $C_{10}H_{20}O$ and decoic alcohol $C_{10}H_{22}O$ are of the same importance. As stated, decoic aldehyde is one of the bodies to which orange oil owes its main flavor and odor value. It is a magnificent product when properly used. Decoic alcohol likewise proves of service in many instances, but if used in excess the effect will be disagreeable.

Duodecoic alcohol $C_{12}H_{26}O$ and duodecoic aldehyde $C_{12}H_{24}O$ serve the same purpose. In traces they are valuable. Some instances have appeared in print where duodecoic aldehyde has been recommended for sweetening ionone and for producing flowery effects when used in the proportion of 10 per cent. Any manufacturer who employs the product in that proportion will be disappointed, because if he uses pure material he will find that a mere trace is all that is required—more than that will entirely spoil the product. The C_{11}, C_{13} and C_{14} allied aldehydes and alcohols are also valuable when used in traces only.

Grass Oils. From the citrus oils we pass to the East-Indian oils of the Citronella family, which include a number of aromatic grasses. They are known by various names, and while closely related botanically, produce oils of entirely different odor-effects when distilled. They include the oils of citronella, palma rosa, or East-Indian geranium, gingergrass, lemongrass and vetiver. Hundreds of tons of these grasses are distilled annually by the natives in India.

Citronella Oil. Oil of citronella is mostly used for technical applications and for perfuming laundry soaps. Chemically, it is a source of the important terpene alcohol, geraniol, a constituent of rose oil. It also contains an aldehyde, citronellal $C_{10}H_{18}O$, closely related chemically to citral, the aldehyde of lemon oil, which serves as a raw material for building up other materials by synthesis.

Palma-rosa Oil. Oil of palma-rosa, or East-Indian geranium oil, is likewise of importance, as it contains a large proportion of geraniol, which is isolated from the oil chemically and finds extended application. The oil itself is used as a soap perfume. Oil of gingergrass, so called up to recent times, was thought to be an adulterated palma-rosa oil, but has been proven to be a distinct essential oil, distilled from a different species of grass. It finds application principally in scenting soaps.

Vetiver Oil. This oil, also known as cus-cus, kusa or kus, is one of the oldest known perfume odors, and still enjoys great popularity. It is distilled from the root of Andropogon muricatus or squarrosus, an East-Indian grass. The oil made in India is usually distilled with sandalwood,

but the root is exported and worked up principally in European factories. The yield of oil ranges from 0.45 to 0.92 per cent. The Réunion oil is much inferior in odor and has a different chemical composition. Even the best oil contains some constituents having a disagreeable odor, furfural, diacetyl, etc. It is purified chemically and may then be used in perfumes of the highest grade. When employed in very small proportions it gives a most charming perfume effect and the fine character of many modern popular odors of the Oriental type is due to this constituent.

Lemongrass Oil. Oil of lemongrass is of great value, because this contains, as previously mentioned, a large proportion of citral $C_{10}H_{16}O$. Citral is not only one of the active principles of oil of lemon to which the main flavor is due, but may be chemically converted into other derivatives which are of much greater value in perfumery. Citral may be condensed with acetone, by any alkaline-condensing agent, forming a ketone derivative known chemically as pseudo-ionone, which by treatment with acids is converted into ionone. Many isomeric substances are produced commercially and find extended application.

Ionone. Ionone $C_{13}H_{20}O$ is a direct derivative of the benzene series. The acid treatment converts the chain formula of the aliphatic series into an aromatic derivative by closing the chain into a benzene ring. Ionone exists in a number of isomeric forms, each of which has a slightly different odor. Many derivatives of ionone have been made. The name " ionone " having been trade-marked at the time the original patent (now expired) was applied for, in 1893, these violet ketones are marketed under various trade names, as iovionol, neoviolone, ional and many others. This has caused some confusion as different products are marketed under the same name. For instance, iralol has been used erroneously for ionone, but properly refers to methyl ionone, a constituent of artificial orris oil. The conversion of pseudo-ionone by means of acid gives rise to many impurities having a disagreeable odor. Consequently these ketones are on the market in all possible qualities, from those which are almost useless, on account of imperfect purification, to products which have a charming floral odor and are applicable for the finest perfumery purposes. Ionone is an isomer of irone, the active principle of the essential oil of orris root.

Orris Oil. Orris root, or the iris of Italy, when distilled, yields an essential oil containing about 90 per cent of myristic acid and about 10 per cent of active perfume substances, of which irone $C_{13}H_{20}O$ is the main constituent. An absolute orris oil free from the fatty acid is also sold, being from 8 to 10 times as strong. Methyl iovionol or iralol $C_{14}H_{22}O$ is a basic ketone having a very sweet and powerful orris odor. Other synthetic orris products are available which even duplicate the valuable fixing properties of the root and are entirely free from the odorless myristic acid found in the natural oil.

Violet Odors. Ionone, as well as irone, popularly represents the violet odor, but as a matter of fact many other substances contribute

to the violet perfume. The manufacturer who thinks he can get a violet by merely dissolving a basic ketone like ionone, iovionol, iralol, irone or orris oil in alcohol is doomed to disappointment, because the other substances are missing which contribute the life-like character and really produce the complex odor-effect which the public knows as violet.

Ionone bears the same relation to the violet odor as geraniol does to oil of rose. Alone it lacks character and life. Synthetic violet-flower oils are used in enormous quantities and may be had in all shadings of this most popular flower perfume; even the so-called "green" odor of the leaf has been reproduced by synthesis with entire success.

Cassie or Acacia Odors. These blossom oils belong to the violet series, but contain as added constituents the methyl esters of salicylic and methyl salicylic acids, methyl-eugenol and other bodies. Both natural and synthetic blossom products are available, which are used extensively and have a most delightful flower perfume. Mimosa also belongs to the cassie type perfumes.

Sandalwood Oil. Oil of sandalwood has been known for many years and has always been highly esteemed in the Orient. Sandalwood itself is an ancient constituent of incense, and the trade in this rare wood is so valuable that it has been monopolized by the Indian government, auction sales being held at regular periods, under supervision of East-Indian officers. But little of the wood is distilled in the Indies; the greater part is exported to Europe and America, where the oil is produced by modern methods. The principal portion of the oil is known as santalol, a rather complex chemical substance which is both alcoholic and aldehydic in nature and consists of a number of distinct chemical individuals.

Santalol. Santalol is much more valuable to the perfumer than sandalwood oil because it represents only the useful portion of the oil, as the ill-smelling constituents have been removed. From some of the fractions of sandalwood oil the writer succeeded in isolating portions which have odors almost identical with certain fractions obtained from oil of patchouly, showing that these oils, produced in the same climate by a tree and herb which have no botanical relation, contain similar compounds.

Cedar Oil. The cedar-like odor of oil of sandalwood has often led to its adulteration with oil of cedar, which is much cheaper and may be had in unlimited quantities. Much cedarwood oil is distilled from the sawdust or shavings produced in manufacturing lead pencils. A finer grade finds a limited market, being used in microscopical work.

Juniper Oil. Cedar is a member of the Juniper family. Juniper berries and their oil have long been used for making gin and for flavoring. The berries have also a historical interest since in some sections of Central Europe, the custom prevails, when a death occurs in a house, of roasting the berries in a red-hot pan, so as to have the odor diffused throughout the rooms. Apparently this is a tradition which has been handed down

from pagan times, since juniper berries formed part of the sacrificial offerings of the early Teutons.

Turpentine Oil. Juniper oil contains a considerable proportion of terpene and this brings us to the field of turpentine and allied products. Turpentine is a widely used solvent and is becoming scarcer each year, so that lately even the old stumps have been utilized to produce a cheap grade. While not a perfume material, the oil is certainly an essential oil and it also serves as a source for some constituents of our most valued flower odors.

Terpineol and Derivatives. Turpentine may be hydrated, forming terpene hydrate, which in turn, by treatment with acids, may be converted into terpineol. This is a terpene alcohol which exists in many of the finest flower oils, though in numerous modifications, widely varying in physical properties, optical rotation, boiling-point and melting-point and differing just as widely in odor. The common terpineol, much used as a soap scent, is a syrupy oil looking like glycerine. Purified products are also marketed and are invaluable in fine perfumery. (Terpineol Blanc, Muguet, Muguet Blanc, Muguet Ideal, etc.) Isomeric modifications of terpineol are present in lilac, tuberose, mimosa, ylang ylang, lily of the valley, and many other exquisite flower oils.

Lilac-flower Oils. Terpineol bears the same relation to these very popular blossom oils as geraniol to oil of rose. Lilac flowers contain many of the other chemical constituents we have already described. Lilac-flower products are obtainable in many shadings of this odor suitable for many different purposes. The so-called French lilac is merely a variation combining lilac and hyacinth odors.

Eucalyptus Oils. In Australia, we find various members of the Eucalyptus family. They yield oils differing very much in chemical composition and odor, and the exact species of tree from which the oil was obtained should always be mentioned. The ordinary commercial eucalyptus oil owes its medicinal effect principally to a body chemically known as eucalyptol or cineol $C_{10}H_{18}O$. Eucalyptol is widely distributed throughout the essential oils in small proportion, but when present in large proportion as in eucalyptus oil, or when concentrated, it has a disagreeable taste and odor. Consequently its use has decreased considerably in recent years, as other medicinal bodies have been found which are not as unpleasant.

Pelargonium or Geranium Oil. Oil of pelargonium is one of the more modern oils and is of considerable commercial importance, as it contains about 70 per cent of terpene alcohols, that is, both geraniol and citronellol, in varying proportions, according to the source. It shows that the same plant will yield other chemical substances when grown in different soils or climates. A number of varieties of pelargonium or geranium are distilled in Algeria and throughout northern Africa, as well as in some of the French islands, especially Réunion, and to a limited extent in southern

France. The plant is common with us as a house-plant, and is known as "rose geranium." The oil is used in perfumery and soap-making, and also serves as the source of the valuable terpene alcohols, which may either be isolated and used as such or changed by synthesis into derivatives having a much higher perfume value. The so-called Turkish or East-Indian geranium oil should not be confused with these pelargonium oils as it is distilled in the East Indies from one of the grasses. See under palma-rosa oil.

Lavender Oil. Oil of lavender is distilled from a member of the mint family, and while quantities are produced in England, the bulk of the product comes from southern France. French lavender oil is commonly valued by the ester content, estimating the mixture of esters as linalyl acetate. The so-called Mitcham or English lavender oil contains less ester but other constituents are present in small proportion which give a different perfume effect. The English oil commands a higher price. This is again an instance where the proportion of one constituent does not determine the value of a perfumery product. It is the quality of the constituents present that influences the value of the oil. Synthetic products are also marketed which impart a similar perfume to the English oil.

New Flower Perfumes. Organic synthesis has likewise made many other flower odors commercially available, which in most instances have not been produced from the flower on a commercial scale. Among the most successful we may mention the flower oils of trailing arbutus or mayflower, cyclamen, honeysuckle, locust blossom, magnolia, sweet-pea, phlox, peony, wallflower, clematis, many tropical orchids, etc.

These are merely a few of the successes of organic chemistry which has supplied materials that have not been commercially made from the plants. Many others are manufactured which can also be made from the flowers, but are so produced only to a limited extent, as for instance, carnation pink, hyacinth, lilac, mimosa, etc.

New Odor Effects. While discussing the subject of recent advances in this field, we must not overlook the many odor effects, made possible by chemical research, which has placed entirely new substances at the disposal of the modern manufacturer and has created new perfume effects so welcome to the public, always clamoring for something novel.

Clove Oil. Cloves, one of the earliest items of trade between the East and West, contain such a large proportion of oil that even the crudest methods give a fair yield. Cloves are the dried, unopened flower-buds of a beautiful evergreen tree. Clove oil is the commercial source of eugenol, which chemically is allyl-methoxy-oxy-benzene $C_{10}H_{12}O_2$. This is present in the commercial oil to the extent of from 70 to 85 per cent. The other constituents are of no commercial importance. Eugenol may be obtained from clove oil by combining it with an alkali, removing the terpenes, setting free the eugenol, and vacuum distilling. Its specific

gravity increases on aging, owing to the formation of resinous or condensation products. Consequently, a perfectly pure material, when freshly distilled, will have a slightly lower specific gravity. By treatment with alkalies, eugenol may be converted into iso-eugenol, which on oxidation yields vanilline.

Vanilline. Chemically, vanilline $C_6H_3(OH)(OCH_3)CHO$ is the methyl ether of protocatechuic aldehyde and forms one of the main flavoring constituents present in vanilla beans. Vanilline alone, however, will not duplicate the entire flavor of vanilla, as it merely represents one of the constituents of the bean flavor. Vanilla beans contain in addition to vanilline, other substances to which the fine flavor of the beans is principally due. Popularly, and quite erroneously, it has been thought that the resinous substances which are present contribute to the flavor. As a matter of fact, the resinous bodies in the bean, when separated, tenaciously hold a small proportion of the active principles, but when perfectly pure, these resins have practically no odor or flavoring value. Synthetic materials are available, however, which duplicate the entire flavor of the finest beans and are free from resins or tannins which contaminate the natural bean flavor.

Allspice Oil (or Pimento). Another oil which contains a considerable proportion of eugenol (65 per cent) is the oil of allspice or pimento, official in the U. S. Pharmacopœia. It is used principally for flavoring. Most of the spices, herbs and other condiments utilized owe their flavoring value to essential oils.

Herb and Spice Oils. Among these, we may mention the oils of mace, nutmeg, caraway, celery, coriander, cumin, fennel, ginger, marjoram, parsley, sage, thyme, and pepper, all of which are more or less complex in composition. Space does not allow their discussion in detail.

Cassia Oil. Another spice oil of importance is oil of cassia, improperly called in the U. S. Pharmacopœia, VIII revision, oil of cinnamon. Oil of cassia owes its main value to cinnamic aldehyde $C_6H_5CH{:}CH.CHO$, which is present to the extent of about 80 per cent. This aldehyde is also produced by synthesis by condensing benzaldehyde with acetic aldehyde.

Cinnamon Oil. Ceylon cinnamon oil is worth about four to five times as much as oil of cassia. It has a finer odor than cassia, and while the content of cinnamic aldehyde is lower, ranging from 65 to 70 per cent, other constituents are present which influence the odor considerably. For this reason, Chinese cassia oil and Ceylon cinnamon oil should not be confused or called by the same name. The odor of cassie also should not be confused with cassia. Cassie is a member of the acacia and mimosa family and belongs to the violet group of odors. See Blossom Oils.

Peppermint Oil. While speaking of the aromatic oils used as condiments or for flavoring, we must not overlook peppermint, which is produced so extensively in America. Oil of peppermint owes its chief value to menthol, an alcohol, having the formula $C_{10}H_{19}OH$, and some

of the esters of menthol, principally menthol acetate. Japanese oil of peppermint is also marketed though often part of the menthol has been previously removed from it.

Fruit "Ethers." While speaking of flavoring oils, we should correct a popular error which early found its way into print and has been repeated many times. Over forty years ago it was noticed that the esters of the fatty alcohols and acids had a fruity character. Old formulas have frequently been reprinted, which give the amateur instructions for the manufacture of pear, banana, strawberry and other fruit oils by merely using these esters (called fruit ethers) in combination with chemical substances which should not be used in food products, such as chloroform, etc. When we consider the number of constituents which contribute to the perfume of flower oils, is it to be supposed that flavors which give aroma to the fruits would be less complicated in composition? It is no doubt true that most fruits contain a small proportion of these fatty esters, but they are present very largely as nature's diluent. They bear the same relation to the fruit flavor as terpenes do to oil of lemon or as the odorless benzyl benzoate to the other substances present in flower oils in smaller proportion. Hence it requires equal study and care to duplicate synthetically any of the fruit flavors, after identifying and producing the bodies to which the real fruit aroma is due. Many of the substances present in flowers are also found in fruits. Methyl anthranilate is an example. This material is present in grapes and contributes largely to the flavor. The same is true of phenylethyl alcohol and its esters, which are more widely distributed in fruits than is commonly supposed.

Fruit Oils. Artificial fruit oils are now commercially available, which imitate the natural flavor remarkably well. Among the more popular flavors marketed we may mention banana, cherry, wild cherry, pear, peach, pineapple, apricot, raspberry, strawberry, etc. Their composition is just as complex as that of the blossom oils, and the fruits contain many of the same constituents as the flowers, but in widely differing proportions. These pure oils should not be confused with *alcoholic tinctures* often maskerading as fruit oils. The shrinkage in volume, when mixed with water will give an indication of the proportion of actual oil present. Or apply a match to a sample. If much alcohol is present the liquid will burn readily. Pure oils undiluted with spirit do not easily ignite from a match.

Future Advances of Science. Much as science has advanced in the last few decades we must appreciate that organic chemistry is still in its beginning. We have learned a great deal. We have found, isolated, and reproduced many of the constituents present in plants, but like the students of biology, before powerful microscopes became available, we wander among undreamed-of wonders. Let all students interested in industrial chemistry remember that every successful advance of the future must be founded on Science. Let us all assist in building the structure, willingly giving

our best toward the ultimate success, even if our individual efforts may be forgotten in years to come.

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CHAPTER XXXII

TURPENTINE AND ROSIN

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THE limited use of the oleoresinous exudate of pine trees dates back many centuries, but the real beginning of the industry on a large scale is closely associated with the discovery of the vast pine forests which extend along the southeastern and southern coasts of the United States from North Carolina to Texas.

These forests lie chiefly in the coastal plain and in the slightly hilly country between the Piedmont plateau and the coastal plain, a strip varying in width from 100–200 miles and characterized by a sandy soil, covered for the most part with "wire grass," this furnishing a beautiful carpet of green in Spring and Summer, but making a serious fire risk in Winter.

The early settlers in eastern North Carolina began the exploitation of their forests of longleaf pine for the purpose of providing tar and pitch for use in the construction of wooden ships, and gradually extended their operations to the collection of crude turpentine which was shipped to Northern cities or England for distillation. At the same time limited operations were being conducted upon the maritime pine in southwestern France between Bordeaux and Bayonne.

Methods of Collection. To receive the crude turpentine the French made use of a hole dug in the sand at the base of the tree. The oleoresin flowing from the wound on the trunk above was collected in these holes. Necessarily by this method much of the material was wasted and rendered impure.

In North Carolina the method of collection consisted of first cutting a large opening, the "box," in the base of the tree, this box serving as a receptacle for the crude turpentine. Each box is then "cornered," a wide chip being removed from each half of the box to provide a surface suitable for directing the flow of crude turpentine to the box. Meanwhile, other laborers are employed in clearing all combustible material from around each tree, "raking." Ground fires are then started to consume the dead wire grass, chips, etc. With the opening of Spring, "chipping" begins. This consists in scarifying each week the trunk of the tree above the "cornered" surface by means of a

" hack," a U-shaped steel tool set in a wooden handle. Attached to this handle is a heavy iron weight to give momentum to the free arm swing used in chipping. After four or five weeks the " boxes " average a good filling and the crude turpentine, " dip," is then transferred to buckets by flat iron paddles, and from the buckets it is collected in barrels conveniently placed in the woods. In the Fall, at the end of the chipping season, the hardened oleoresin, which has gradually collected during the chipping season on the scarified surface of the tree, is removed by scraping, giving thus the name " scrape " to this product, which is sold as " Gum Thus," or distilled. In the following Winter the trees are again raked and the grass fired and in the Spring chipping is resumed at the point on the trunk of each tree where it ceased the previous year. This cycle is usually continued from three to four years, although in early days it was often continued ten or twelve years, the scarified surface extending high on the trunks. Necessarily the yield from such high chipping was largely decreased, owing to the increased distance of flow to the receptacle.

The supply of available timber in North Carolina rapidly decreasing, operations were extended to the virgin forests of the adjoining state, South Carolina. The center of the industry has gradually moved southward and then westward.

French Improvements. The steady growth of the American industry received a serious check during the Civil War. The consequent scarcity of the products was accompanied by an abnormal increase in their value. This enhanced valuation led Hugues, a Frenchman, to propose a less wasteful method for the French forests than the hole dug in the sand. He proposed as a substitute a clay pot holding about one pint. This pot was supported on its bottom by a large nail driven into the tree and on one side of its upper rim by a strip of sheet zinc, approximately 2 by 4 inches, slightly curved and driven into a corresponding upwardly inclined cut in the wood. This spout served to direct the oleoresin into the pot. At first his proposition was scoffed at and the peasants amused themselves by breaking the little pots. It is a pitiful commentary that Hugues died in poverty, but his ideas lived and gradually became adopted in France.

American Improvements. As the knowledge of the new method in France spread to this country, numerous efforts were made to apply similar forms of apparatus to the American system of chipping, but for many years such efforts failed. No less than fifteen patents were issued in the United States on this subject, but no one of them proved a commercial success.

Twelve years ago a series of field experiments on a small scale in the turpentine forests of South Georgia was begun. One feature of these experiments was the use of a modification of the Hugues system, consisting of two separate metallic gutters, inserted in upwardly inclined cuts in the tree, along which the oleoresin flows. The upper and shorter gutter

is separated at its lower end about 1 inch from the lower gutter and empties into it. The lower gutter extends from 2 to 3 inches beyond the center of the angular scarified surface formed in chipping and serves as a spout to convey the oleoresin to a cup suspended from a nail just below the end of the gutter. These cups are made of either well-burned clay or galvanized iron, and have a capacity of 1 quart.

Attracted by the promising character of these preliminary experiments, the United States Bureau of Forestry began a series of field tests of the apparatus on a large scale, the work being under the immediate supervision of the writer. Before the end of the first season of testing it was evident that the apparatus was a practical success, and the results attained, both as to quantity and quality of oleoresin, justified the hope of immediate commercial introduction of the system. But the habits of long years made difficult the adoption of such an innovation. This ultra-conservatism was slowly overcome and the adoption of the new system spread rapidly. Only a few years more will be required to witness the complete replacement of the "box" by the "cup" system in American forests. A detailed account of these experiments is given in Bulletin 40 and Circular 34 of the United States Bureau of Forestry.

With the main points at issue settled, namely, improved yields both in quantity and quality of the products and preservation of the trees, other forms of apparatus were devised to meet the objections of some of the operators to certain points in the cup and gutter system. Many of these have never proved practical, but some have been introduced on a considerable commercial scale.

The United States Forest Service has made further experiments of more conservative treatment of the trees in chipping. Comparative studies of the yield from deep and shallow chipping showed that the latter gave a greater yield during a period of four years of operation. Other experiments showed that a less rapid rate of ascent of the trunk also gave larger yields, and experiments combining these several modifications of present practices showed a largely increased yield. A final set of experiments pointed clearly the rational way to a perpetuation of the naval stores industry in America. The details of this investigation are given in Bulletin 90 of the United States Forest Service.

The Industry in Other Countries. There is no need of any especial consideration of the Spanish industry, which has developed considerably during the past decade. The operations are essentially the same as the French, and the same species of pine, Pinus Maritima, is exploited.

In Austria the industry is more limited and is even more destructive than by the old American system, a "box" being cut in the base of the tree, *Pinus Laricio*, and the trunk of the tree scarified for at least 50 per cent of its circumference, the oleoresin being directed towards the center of the scarified surface by thin wooden strips inserted in downward cuts in the tree.

In Russia the chief tree exploited is *Pinus Sylvestris*. Climatic conditions do not admit of the usual process of collecting the crude turpentine at regular intervals. Instead, the trees are scarified in Spring over a space about 3 feet high and almost encircling the tree. During the year a mass of hardened rosin collects on this surface. In the Winter it is scraped from the tree and distilled for its volatile oil and resin. This process is repeated for five years. The tree is then felled and the resinous portion of the tree subjected to destructive distillation. In other districts no effort is made to collect the rosin from the trees annually, but this is allowed to remain until the end of the fifth year of scarification. The tree is then felled and that part containing the rosin distilled first at a low temperature to obtain the volatile oil, then at a more elevated temperature to obtain tar and charcoal by destructive distillation of the wood.

The spirits of turpentine from Germany, Sweden, and Finland seems to be a product solely of the destructive distillation of resinous wood.

The production of naval stores in India and other tropical countries is at present carried out on only a small commercial scale.

Distillation. In the early days of the North Carolina industry, no effort was made to distill the product, but gradually it became clear that it would be better to separate the crude turpentine into spirits of turpentine and rosin by distillation in the woods. For this purpose iron stills were used at first, but results were unsatisfactory until the introduction of copper stills, which were less liable to crack and could be heated with greater uniformity and better control.

Only slight advances in this art have since been made in America. The uniform process consists in the use of a large copper kettle and condensing worm. The charge for a distillation averages 9 to 10 barrels of crude turpentine. The kettle is heated by free flame and during the distillation a small stream of hot water from the top of the condenser tub is admitted through an opening in the upper part of the kettle, thus facilitating the removal of the volatile oil. The condensed spirits of turpentine and water separate in the receiver, owing to difference in specific gravity, and the lighter spirits of turpentine is transferred to oak barrels, well coated with glue on the inside. No effort is made to redistill this product, and it always comes upon the market contaminated by a small amount of resin carried over mechanically during distillation. After most of the volatile oil has passed off, the still cap is removed, excess water in the kettle boiled off, and the molten rosin drawn off through a tap in the bottom of the kettle onto a coarse wire filter, then through a second filter of fine mesh wire overlaid with cotton batting. The molten rosin is then dipped into wooden barrels luted with clay, and solidifies on cooling. In this condition it is shipped to market.

The usual method of controlling the distillation is by the sound heard at the mouth of the condenser worm. Within the past three years a num-

ber of American operators have substituted for this method that of thermometer control with very excellent results.

In France, much more progress has been made in the art of distillation. Among the French distilleries there are three distinct types: first—a system closely resembling the American; second—distillation solely by steam in steam-jacketed vessels; and third—a mixed system in which there is direct contact of fire with the kettle during the first stage of the distillation, then replacement of this by mixed injection of steam and hot water. By this means, a constant temperature is maintained, enabling the complete removal of all spirits of turpentine without danger of scorching the rosin.

Crude Turpentine and Its Distillation Products. The oleoresin, crude turpentine, as it first issues from the wounded tree is a limpid viscous liquid. Crystallization of the contained acids soon begins and the mass finally becomes a crystal broth. The composition of this mass as determined on a 10-barrel charge at the still showed:

Spirits of turpentine	19.57	per cent
Rosin	66.64	"
Impurities, clips, sand, etc.	4.67	"
Water (determined by difference)	9.12	"
Total	100.00	"

The " scrape " collected from the scarified faces of the trees at the end of the chipping season showed an average of about one-half the content of spirits of turpentine as compared with crude turpentine.

The volatile oil, spirits of turpentine, consisting largely of pinene, when freshly distilled from " virgin " gum has a pleasant fragrant odor, which readily changes to a sharp pungent odor under the oxidizing action of exposure to atmospheric oxygen.

No definite physical constants can be given for spirits of turpentine, as variations occur due to preponderance of the crude turpentine in collection from the species of pines under operations. In America these are *Pinus Palustris* (Longleaf pine) and *Pinus Heterophylla* (Cuban or Slash pine). Even in the same species marked variations, especially of the optical rotations, have been found.

The specifications for spirits of turpentine as issued by the United States Navy Department are as follows:

Navy Deparmtent Specifications

Turpentine

1. *General Specifications.* General Specifications for Inspection of Material, issued by the Navy Department, in effect at date of opening of bids, shall form part of these specifications.

2. *Quality.* The turpentine shall be (*a*) either a properly prepared distillate from pine oleoresins, commonly known as gum turpentine or spirits of turpentine; or (*b*) that obtained from resinous wood by extraction with volatile solvents, by steam, or by destructive distillation, and commonly known as wood turpentine.

3. *Appearance.* The turpentine shall be clear and free from suspended matter and water.

4. *Color.* The color of the turpentine shall be such that a depth of not less than 50 mm. shall approximately match a No. 1 Lovibond glass. This color is recognized as "standard" in the naval stores trade, and shall be determined as follows:

METHOD. Fill a 200-mm., perfectly flat-bottom colorimetric tube, graduated in millimeters to a depth of from 40 to 50 mm., with the turpentine to be examined. Place the tube in a colorimeter and place on or under it a No. 2 yellow Lovibond glass. Over or under a second graduated tube in the colorimeter place a No. 1 yellow Lovibond glass, and run in the same turpentine until the color matches as nearly as possible the color in the first tube. Read the difference in depth of the turpentine in the two tubes. If this difference is 50 mm. or more, the turpentine is "standard."

5. *Specific Gravity.* The specific gravity of the turpentine shall be not less than 0.862 nor more than 0.872 at 15.5° C.

6. *Refractive Index.* The refractive index shall be not less than 1.468 nor more than 1.478 at 15.5° C.

7. *Initial Boiling-point.* The initial boiling-point shall be not less than 150° nor more than 160° C.

8. *Distillation.* Ninety per cent of the turpentine shall distill below 170° C.

METHOD. Use an ordinary Engler flask and condenser, and heat the flask by placing it in a glycerin or oil bath of the general type described in Bulletin No. 135, Bureau of Chemistry. Fit the flask with a thermometer reading from 145° to 200° C. in such a way that the mercury bulb shall be opposite the side tube of the flask and the 175° mark below the cork. Place 100 cc. of the turpentine to be examined in the flask, connect with the condenser, insert stopper-bearing thermometer, heat the oil bath, and conduct the distillation so that the distillate passes over at the rate of 2 drops per second. Note the initial distilling temperature and the percentage distilling below 170° C.

9. *Polymerization.* The polymerization residue shall not exceed 2 per cent, and its refractive index at 15.5° C. shall not be less than 1.500.

METHOD. Place 20 cc. of exactly 38/N (100.92 per cent) sulphuric acid in a graduated, narrow-neck Babcock flask, stoppered, and place in ice water and cool. Add slowly 5 cc. of the turpentine to be tested. Graudally and carefully mix the contents, cooling from time to time, and not allowing the temperature to rise above about 60° C. When the mixture no longer warms up on shaking, agitate thoroughly, and place the

bottle in a water bath and heat from 60° to 65° C. for about 10 minutes, keeping the contents of the flask thoroughly mixed by vigorous shaking five or six times during the period. Do not stopper the flask after the turpentine has been added, as it may explode. Cool to a room temperature, fill the flask with concentrated sulphuric acid until the unpolymerized oil rises into the graduated neck. Centrifuge at about 1200 revolutions per minute from 4 to 5 minutes, or allow to stand for 12 hours. Read unpolymerized residue, notice its consistency and color, and determine its refractive index.

10. *Flash-point.* The turpentine shall not flash below 34° C. when tested in an Abel's closed tester.

11. *Basis of Purchase.* Turpentine will be purchased by the commercial gallon.

12. *Determination of Quantity.* (*a*) *Certificate.* Turpentine delivered in barrels shall be accompanied by an official gauger's certificate whenever practicable. Such deliveries will be accepted for the number of gallons shown on certificate, unless there is evidence of loss by leakage or other shortage in transit, in which case the number of gallons in short barrels shall be checked at the delivery point.

(*b*) *Weight.* Turpentine delivered in 5-gallon cans or in barrels, when not accompanied by an official certificate, will be checked by weight. When deliveries are made in cans the gross weight of 10 per cent of the total number of cans shall be taken to determine the average gross weight; the tare weight of 1 per cent of the total number of cans shall be taken to determine the average tare weight; and the total net weight delivered will be obtained from the average weight thus found. When deliveries are made in barrels 10 per cent of the total number of barrels will be taken to verify the net weight delivered; and if the markings are found incorrect the whole delivery will be checked at the contractor's expense. The number of pounds per gallon shall be determined by multiplying the specific gravity of the turpentine at 15.5° C. by 8.33 pounds, the weight of 1 gallon of water (231 cubic inches) at 15.5° C.; and the number of gallons delivered will be obtained by dividing the total net weight by the number of pounds per gallon.

Containers

13. *General.* Turpentine shall be delivered in 5-gallon tin cans, packed two cans per case, or in barrels, as required.

14. *Cans and Cases.* Cans and cases shall be in accordance with the latest issue of Navy Department Specifications for Five-gallon Tin Cans and Shipping Cases.

15. *Barrels.* Barrels shall be made of oak or other suitable hardwood, thoroughly kiln dried, and shall conform in all respects to the requirements of Shipping Container Specification No. 10 of the Interstate Commerce Commission.

16. *Marking.* (*a*) *Cans.* Each can shall be labeled with the name of the material, the quantity contained, and the name of the manufacturer.

(*b*) *Cases.* Each case shall be marked with the name of the material, the name of the contractor, and the contract or requisition number under which delivery is made.

(*c*) *Barrels.* Each barrel shall be marked with the name of the material, the gross, tare, and net weights, the name of the contractor, and the requisition or contract number under which delivery is made.

Specifications, where obtainable.

NOTE. Copies of the above specifications can be obtained upon application to the Bureau of Supplies and Accounts, Navy Department, Washington, D. C.

References. C. & R., Z52T2b–M, May 29, 1917; S. & A., 380–868.

The rosin, left after removal by steam, of the volatile oil varies in color from a very deep red to a light yellow. The lighter the color the more valuable the rosin, as indicated by the daily market quotations of these different grades of rosin.

The bleaching of the lighter shades by prolonged exposure to direct sunlight is carried out in France on a large scale. The deepening of the color of rosin is due primarily to the oxidizing action of the atmosphere, and the contamination of the fresh oleoresin as it flows over the already oxidized material adhering to the scarified surface of the tree.

Rosin is composed chiefly of acids, such as abietic acid, $C_{19}H_{28}O_2$, approximately 94 per cent and so-called unsaponifiable matter, "Resene," approximately 6 per cent. The acid number of rosin varies with different samples, but is approximately 160, while the so-called ester number is approximately 7.

Rosin has no definite melting-point, beginning to soften about 70° C. Its specific gravity is approximately 1.07.

Wood Spirits of Turpentine. Among the various departments of the naval stores industry in America none has had a more varied and interesting career than that of the production of " wood spirits of turpentine " by destructive distillation of resinous wood. Years ago considerable capital was invested in plants for utilizing the by-products formed during the destructive distillation of " fat lightwood." None of the plants were commercially successful and for a while nothing was heard of the industry. But with the increase in price of spirits of turpentine resulting from the formation of the Turpentine Operators Association in 1902, a fresh impetus was given to the " wood spirits of turpentine " industry. At first somewhat crude methods of destructive distillation were advocated, and as the promoters of this industry appealed largely to local interest in having stumps for distillation removed from the fields suitable for cultivation, a double impetus was received. Much enthusiasm was aroused, and a number of plants constructed. But the industry received a serious blow in the refusal of the varnish makers to use the impure " wood spirits of turpen-

tine" manufactured, by the failure to find a market for many of the heavier oils and the coke, and by the destruction by fire of many of the improperly constructed plants.

The price of spirits of turpentine continued to rise and led to the development of the steam extraction process for manufacture of wood spirits of turpentine. After thorough grinding, the wood is treated in iron retorts with steam, and the volatile oil distilled, no effort being made to obtain any other product. By one redistillation of the product a very high grade spirits of turpentine is obtained, equal, if not superior, to that from the living tree. Unfortunately, the yield is not sufficiently large to make the process remunerative.

Quite a different process is employed by those plants which utilize a bath of molten rosin for removal of the spirits of turpentine from the wood, with subsequent distillation of the volatile oil from this bath. Such plants seem to have met with a fair measure of success.

More recently, extraction processes have been developed which employ low-boiling petroleum products as the extractive. Such plants recover both the spirits of turpentine and the rosin from the ground wood, and have a great advantage in the present very high value of rosin. These plants are also utilizing the refuse from the straining of rosin at the distilleries in the woods, a product formerly burned on the waste piles, but now bringing nineteen dollars per ton. This method is adding a considerable amount to the annual output of rosin.

The most recent development is a plant for destructive distillation of wood in retorts heated by jackets filled with high-boiling petroleum fractions. By this means the fire risk is practically completely eliminated and the results indicate that by means of the complete and ready temperature control of the oil jacket larger yields of better products can be obtained.

Annual Production of Naval Stores. No subject connected with the naval stores industry admits of so little accuracy of statement as does that of statistics on the total annual production. The most careful estimates are at best only approximations. This is unfortunate, for in the past it has frequently led to speculative manipulations of the market and the temporary establishment of values which had no legitimate basis depending on supply and demand.

The following table of annual production in normal times is given, therefore, as an approximation only, but it is believed to be a reasonably accurate approximation:

	Spirits of Turpentine Barrels (52 Gallons)	Rosin Barrels (500 Lbs.)
America	600,000	2,100,000
France	100,000	350,000
Spain	25,000	87,500
Austria	3,000	10,500
Other countries	50,000 (?)	(?)
Total estimated production	778,000	2,548,000

Future of the Industry. During the past few years the statement has frequently been made that from present indications the naval stores industry must cease to exist, at least as a large industry, within the next twenty years. While it is true that there are danger signals which must be heeded, such pessimistic views do not seem to be well grounded.

Certainly in France and consequently in Spain, where the same system is in operation, the industry has been placed upon a self-perpetuating basis.

In America we have been prodigal with our wealth of virgin forest. But it must be remembered that until the last decade these forests have had a very low commercial valuation. The average price for well timbered lands in our Southern States not many years ago was approximately one dollar per acre, land, timber, and all. Indeed, the popular term applied to all holders of large tracts of such lands was "land poor," as expense of taxation, protection, etc., exceeded any hope of probable profit. This condition was largely due to lack of transportation facilities, insecurity of title, low price of naval stores and lumber, lack of knowledge of the farming value of much of the land on which these forests stood, and the belief that the forests were inexhaustible.

Now conditions have entirely changed. Railroads penetrate every portion of the territory, titles have been cleared, prices of naval stores have brought wealth to the operators, the lumbermen from Michigan, Wisconsin, and other Northern States have turned from the rapidly disappearing white pine forests of the North to those of the Southern yellow pine; where forests once stood farms have been developed which surpass in fertility any other portion of the Southern States, and a clear knowledge has been gained that the forests are by no means inexhaustible. Furthermore, the spirit of conservation of natural resources has made itself felt in this field as well as in those of minerals, water-power, etc.

The consequence of these changes has been a very rapid enhancement in the value of such holdings. And with increased valuation comes naturally the desire to protect and use conservatively. Unquestionably, the stand of virgin forest will still further diminish, for the demand for farm lands is active, the call for lumber imperative, and the danger of tropical storms along the Gulf Coast ever present. With such diminution in supply will come still further enhancement in values and still more conservative methods of operation.

So much for the present stand of virgin forest. If the situation was limited to this alone, the outlook might be considered gloomy. But it must be remembered that there are vast tracts of cut-over lands in portions of the Southern States whose clay sub-soil lies so deep that the lands are not suited to agriculture. On such lands the longleaf pine, with its long tap root, prospers. Magnificent forests once covered every acre of such lands and fortunately tree planting is not required to reproduce such forests. Nature alone will again cover this territory with a wealth of forest, provided nature is given an opportunity; for the most superficial

observer who travels through this territory will testify that where conditions have been favorable natural reproduction has brought again splendid, though small, young forests.

Against this willingness of nature to restore this rich heritage to us, stand three agencies.

First, and of least importance: The consumption by hogs of the delicately flavored and nutritious feed of the longleaf pine. This is a real factor in certain somewhat restricted districts. The constantly spreading sentiment for " stock laws " will check this evil.

Second, and of the very greatest importance: The destructive action of the ground fires, which annually sweep over the entire turpentine belt. Such fires destroy the myriads of young seedlings which can readily be seen springing up in the wire grass which surrounds them on every side. The seedling devotes the greater part of its early energies to sending down its long tap root through the deep sands rather than to strengthening its stalk above ground; hence, in most cases, it is not able to withstand the constantly recurring ground fires. The doctrinaire may rail against the evils of such firing of the woods, but from one who has lived among the turpentine camps there comes no word of reproach against the turpentine operator who " burns the woods." His all is invested on the outer surface of his trees. A serious outbreak of fire during midseason means financial ruin. The carelessness and sometimes viciousness of laborers is too serious a risk to run with a mass of dead wire grass covering every foot of his territory. Naturally he protects himself by burning this grass when he is prepared for it, after " raking season."

Where then is the hope for reforestation? In the realization of the value of the waste cut-over lands where turpentine operations cannot be carried on for lack of timber. Such lands have now but little value, but the lesson of France shows that even there a reasonable income begins from artificial reproduction within a period of twenty years and then rapidly increases. With our warm Southern climate the prospect for rich returns from such investments should be even greater than in France.

Third. The greed of man. If we are to have a self-perpetuating industry, even stock laws and the reforestation of waste lands will not avail if a practice on the part of turpentine operators during the past two years continues. The abnormally high price of spirits of turpentine a few years ago led to a wild scramble for timber for increased operations. At the same time the efficiency of the " cup " system was just gaining wide recognition. Realizing that a tree too small to have a " box " cut in it could be worked with a cup hung upon it, the operators throughout the whole region proceeded to cup every small tree to which access could be gained. In many cases new farms were opened on old abandoned territory where natural reproduction had furnished thrifty young forests. The result was overproduction of crude turpentine. The temporary benefit to the consumers in the drop in values following this overproduction was

dearly bought, for the price was the destruction of young forests which, in time, should have produced their full share of the world's need of spirits of turpentine and rosin. Common sense must and will govern in this matter. It is only necessary for the operators to realize that the yield from such saplings does not meet the cost of production, then the practice will cease.

Surely the above considerations justify an optimistic view of the future of the naval stores industry. But experiment, demonstration, statistics, and knowledge of progress made in other lands, must lead the way for the man in the woods.

CHAPTER XXXIII

RESINS, OLEO-RESINS, GUM-RESINS, AND GUMS

ALLEN ROGERS

Source. These products are all derived from exudations of plants and as a rule are oxygenated bodies. When mixed with certain percentages of the natural essential oil accompanying them, they are known as oleo-resins or balsams. If mixed with mucilaginous matter they are harder and known as gum-resins. Gums are amorphous bodies which either dissolve in or gelatinize with water, but they are insoluble in alcohol. True resins are distinguished from gums in that they are all insoluble in water, free from odor or taste, form compact masses, and are usually of an aldehydic or acid nature. Fossil resins are generally found in the earth in the form of irregular lumps, often containing perfect specimens of fossil insects and leaves.

Amber. Amber is a fossil resin occurring as small masses in alluvial deposits in various parts of the world. According to Goefert it represents the resinous exudation from about fifty different kinds of coniferous trees. It is found chiefly in Prussia along the shores of the Baltic where it is thrown up by storms; or in some localities it is even mined. Large deposits also occur in some of the lakes on the eastern coast of Courland. Small deposits have been found in New Jersey and Maryland but not of sufficient magnitude to be of commercial importance. The largest single mass of amber ever reported weighed 13 lbs. It is usually associated with lignite and often contains the fossil remains of insects and vegetation.

Amber is a brittle solid, permanent in the air, and susceptible to a very high polish. By application of friction it becomes negatively electrified. Its color is usually from light to deep brownish yellow, although sometimes a reddish brown or bluish. Tasteless and odorless when cold, it gives off a peculiar aromatic odor when heated. It is generally translucent, though sometimes transparent or opaque. Water or alcohol have little effect on it. When heated in the air, it softens and finally melts at 286° C., which property makes it of value in the manufacture of varnish. From its distillation several products result, among them succinic acid, esters, and oil of amber. Amber is used in making high-grade varnish, as well as extensively in the manufacture of tobacco pipe stems and articles used for ornamental purposes.

Animé. The substance known as *gum animé* is a resin supposed to be derived from the *Hymenœa Courbaril*, a leguminous tree of South America. The resin exudes from wounds in the bark and is also found under ground between the principal roots. It occurs in small irregular pieces of a pale yellow color, sometimes of reddish cast. It softens in the mouth, and when in a powdery condition adheres to the fingers. It readily melts on being heated, giving off an agreeable odor. It consists of a small amount of volatile oil and two resins, one being soluble in cold alcohol and the other insoluble. Animé was formerly used to quite an extent in the preparation of ointments and plasters; but at present is only employed as incense or in the manufacture of varnish.

Burgundy Pitch. When incisions are made in the Norway Spruce a sap exudes, which is collected in small troughs, or holes dug at the foot of the tree. It is purified by filtering through straw and allowed to harden, subsequently being boiled with water to remove the volatile oil.

Copal. This is a resinous substance derived from the exudation of several varieties of trees indigenous to the East Indies and South America, as well as parts of Africa, the Philippine Islands, and other places. The gum is sometimes taken directly from deposits on the tree or is found imbedded in the earth. That variety of copal known in commerce as *Gum Zanzibar* is found usually under ground. Another variety with indented goose-flesh surface, known in the English market as animé, is dug from the earth.

Copal varies in appearance and properties depending upon the source from which it is derived. It appears in roundish, irregular, or flattish pieces, often with a rough indented surface due to sand impressions while it was in a soft condition. In color it ranges from colorless to yellowish brown; it is more or less transparent, very hard, odorless, tasteless, and has a specific gravity of from 1.045 to 1.130. It is insoluble in alcohol, partly soluble in ether, and slightly soluble in oil of turpentine. When heated it melts, giving off gases to the amount of 15 to 20 per cent of its weight. Its properties are changed by this treatment so that it becomes more soluble in alcohol, ether, and oil of turpentine This characteristic renders it, like other resins, suitable for the preparation of varnish.

Dammar. This is a resin which exudes in drops from a coniferous tree, *Agathis Loranthifolia*, and is collected after it dries. It is soluble in essential oils, in benzol, and to a slight degree in alcohol and ether. Owing to its light color and ready solubility in turpentine, it finds extensive application in the manufacture of light-colored transparent varnishes.

Dragon's Blood. This is a resinous substance obtained from the fruit of several species of small palms growing in Siam, the Molucca Islands, and other parts of the East Indies. An exudation appears on the surface of the ripe fruit, which is separated by rubbing, by shaking

in a bag, by exposing to steam, or by decoction. The finest product results from the first two methods. It comes on the market in two forms: either as small oval drops (*tear dragon's blood*) covered with the leaves of the plant and connected in a row like beads; or in cylindrical sticks 18 ins. long and about ½ in. in diameter, covered with palm leaves and bound with slender strips of cane. An inferior product, prepared by boiling the fruit in water, is in the form of flat circular cakes (*cake dragon's blood*).

Dragon's blood is odorless, tasteless, insoluble in water, but soluble in alcohol and ether, also soluble in the volatile and fixed oils, forming red solutions. Its principal use is in the coloring of varnish.

Elemi. This resin is obtained by making incisions into the trees, through which the juice flows and concentrates on the bark. Elemi comes on the market either as soft Manila elemi or hard Brazilian elemi, being of various colors from light yellow to greenish white. It is soluble in alcohol and other solvents, its chief use being to impart toughness to varnishes made from harder resins.

Guaiacum. This resin is the concrete juice of the tree *Guaiacum Sanctum*, obtained by several different methods. The simplest method is that of spontaneous exudation, or by making incisions in the trunk. Another method is to saw the wood into blocks, bore holes in them longitudinally, place one end of the block in the fire and collect the melted resin which flows out at the opposite end. The usual plan, however, is to boil the chips and sawdust with a solution of common salt and skim off the substance rising to the surface. Guaiac appears in the market as irregular lumps often mixed with small fragments of bark and sand. The purest form comes in small lumps, "*tears*," which result from natural or induced exudation.

Kauri. This is an amber-like resin, varying from light cream to brownish yellow in color. It is the result of exudation from the tree *Agathis Australis*, and is dug in large quantities from the ground in New Zealand. It is used very extensively in varnish-making, and, like copal, must be first heated or "*run*" before it becomes soluble in oils.

Mastic. This is a resinous exudation from the *Pistacia Lentiscus*, a tree cultivated in the Grecian Archipelago. Incisions are made in the trunk and large branches, from which the juice on exuding either hardens on the bark in tears or drops to the ground, where it is caught on cloths. It is of a light yellow color and nearly odorless. It is soluble in alcohol up to about 90 per cent, and is used to quite an extent in the preparation of spirit varnish.

Sandarac. This resin resembles mastic very closely and comes on the market in the form of tears. It is more soluble in alcohol, however, and is employed largely in the preparation of transparent varnish.

Oleo Resins. The most important members of this class are *Benzoin*, *Peru*, *Tolu*, and *Storax*. They are all mixtures of resins with essential

oils, and consequently have a much softer consistency than the resins. They are used especially in pharmacy, and, since they have practically no industrial application, will not be considered in detail in this chapter.

Gum Resins. The more important members of this class are *Ammoniacum*, *Asafoetida*, *Euphorbium*, *Galbanum*, *Gamboge*, and *Myrrh*. They are mixtures of gums and resins, form emulsions with water, and are all largely used in pharmacy, gamboge being also employed as an orange red pigment.

Acacia. Both *Gum Arabic* and *Gum Senegal* are included under this head, as they are derived from plants of the acacia family usually found in Africa. It forms lumps of various sizes with color ranging from white to reddish brown. It is soluble in both cold and hot water and is used in the preparation of emulsions, in thickening ink, in water-colors, textile-printing, sizing cloth, and in the preparation of mucilage.

Agar-Agar. This is also known as *Bengal Isinglass* and *Japan Isinglass*. It is derived from certain algae from which it is obtained by boiling in water. It comes on the market as long white masses. It is used as a sizing for cloth and as a culture medium for bacteria.

Iceland Moss and Irish Moss. These are derived from a form of seaweed which, on boiling with water forms a jelly much used in the textile, and leather industries as well as for edible purposes.

Tragacanth. This is a gummy exudation from *Astragalus Gummifer*. It is odorless, nearly tasteless, and of a very light yellowish to white color. It usually comes into the trade in a flaky condition. Placed in water it absorbs a certain amount and swells up very much, forming a soft adhesive paste. If the paste is agitated with more water, it forms a uniform mixture, which, however, will settle out on standing, as only part of the gum goes into solution. It is largely used in calico-printing and for other purposes where an adhesive is required.

CHAPTER XXXIV

SHELLAC

A. C. LANGMUIR

A distinction should be made between shellac and lac. Lac is derived from the Indian term for 100,000 and is significant of the myriad or swarm of insects taking part in its formation. It has been erroneously stated that lac is the dried exudation of a tree, caused by the sting of the lac insect, and is similar to rosin in its origin. As a matter of fact, it is the secretion of the lac insect, and is a product of the assimilation of the tree sap which the insect feeds upon, just as honey and beeswax are produced by the modification of the nectar of flowers by the bee.

Shellac is so called because of its shell-like form, and bears the same relation to lac that flour bears to wheat. It is a manufactured article, and may be manipulated and adulterated, whereas lac is the original resin as gathered from the trees, and cannot be sophisticated.

Lac is found only in north-eastern India and, to a small extent, in the adjacent sections of Assam and Burmah. The shipping-point is Calcutta. The insect producing lac belongs to the scale family (tacchardia lacca), and in the larval form when hatched is about one-fortieth of an inch in length and of a red or orange color. It has six legs, but no wings, and is too small and weak to travel far. It crawls or drops to another twig in the vicinity, but thousands are unsuccessful, through their inability to find a favorable position or a suitable soft, sappy twig which they can pierce with their beaks. As soon as the insect comes to rest it immediately begins to suck up the sap like an animated siphon, and secretes a substance which soon dries around it in contact with the air. They take up positions adjoining one another so that as the cells surrounding the insects grow larger they eventually coalesce, forming an incrustation around the twigs several times as thick as the twigs themselves. The formation of the lac is undoubtedly designed as a protective coating to shield the insect from its many enemies. Monkeys, ants and squirrels feed on the sweet incrustation. Heavy rains, hail storms, droughts, and forest fires work at times serious injuries.

About two and a half months after the period of swarming the male insect matures, and after pushing up the lower edge of its cell crawls out backwards. The female stays in place. The female is provided with

three tufts of filaments covered with a white powder. As the lac gathers around, these filaments act as tubes to supply air and to permit fertilization by the male, who then dies. The female lives about three and a half months longer, continuing to feed on the sap. For this reason the female cells are larger than the male cells, and may be recognized when a cross-section is made. About a thousand eggs are developed by each female, and by the time these eggs are hatched the mother has dried up, leaving only the skin. The new brood escape from the body of the parent by the air-ducts in the lac, and another life-cycle begins. There are two generations each year, the swarming taking place in July and December. Lac may be propagated by cutting off the swarming twigs and tying them to the branches of healthy trees.

Stick-lac. The incrusted twigs are broken into short sections and constitute the stick-lac of commerce. The lac is gathered twice a year by the natives. It is brought to some central point, such as Mirzapore, where it is hand-picked and graded. The principal trees bearing lac are the Kusum and Palas, but some 88 varieties of trees have been recognized as hosts for the lac insect. The kind of tree and the nature of the sap fed on, as well as climatic influences, are undoubtedly factors in the value of the product. Almost nothing is known of the origin of the various varieties of stick-lac.

Seed-lac or grain-lac is produced from stick-lac by crushing, washing, and drying. In this way the wood and a considerable part of the coloring matter is removed. Seed-lac consists of ruby-red or orange-colored grains about the size of wheat.

Lac Dye. If the wash-water from the stick-lac is allowed to settle, lac dye deposits. Before the advent of the synthetic dyes large quantities of this material were shipped to Europe (1,544,480 lbs. in 1880), where it was used as a substitute for cochineal. The trade has now entirely disappeared and lac dye is only seen as a curiosity.

Shellac. To make shellac the workman fills long, narrow bags with dry seed-lac, to which a certain quantity of orpiment, and sometimes rosin, is added. The bag is heated over a charcoal fire until the lac has fused and run through the cloth. By twisting the bag the molten lac is forced out and is scraped off with a metal hook. It is flattened out by stretching over a cylinder filled with hot water. It is then reheated, clasped between the feet and hands, and pulled out into a thin sheet of a light to dark orange color. In good grades any imperfections are flecked out of the sheet by the finger. The edges are broken off and remelted in the better grades.

The sheets are broken into flakes and packed for shipment. This is the form in which lac is commonly seen, and is the material for sale in the paint store.

Shellac is graded in accordance with its color and transparency, flatness and strength of the flakes, and freedom from adulteration. Orpiment

is universally added to produce the light-yellow color demanded by the trade. It varies in amount between .05 and 0.25 per cent.

The better grades of shellac are commonly spoken of as the marks, of which some of the more important are as follows: D.C. (David Campbell), V.S.O. (very superior orange), Diamond I, Double Triangle G., Superfine, Fine, and Good, Standard One, Two and Three, etc. These grades are generally free from rosin.

The lower grade (largely exceeding any of the others in amount) is known as T.N., and may contain 5 per cent and more of rosin, unless marked Pure. The United States standard T.N. does not contain over 3 per cent rosin (U. S. S. A. mark).

The marks and some of the T.N. are packed in wooden cases, lined on the inside with cloth (usually obtained from the bags used for melting seed-lac) and wrapped on the outside with burlap, on which is branded the mark and the initials of the maker's name. The customary net weight is two maunds, or 164 pounds. The T.N. grade is usually shipped in double burlap bags carrying 164 pounds. The route from Calcutta lies through the Red Sea, and the summer shipments are often received in a more or less matted condition, due to the softening of the shellac en route. This is particularly noticeable with the T.N. grade, packed in bags, the pressure and lack of ventilation causing the solidification of the shellac into hard slabs. To describe the condition of the shellac the terms free, caught, matted, firmly matted, and blocked are used.

The yearly output is about 250,000 packages of 164 pounds each —about 41,000,000 pounds. The total imports for the United States were in 1914, 125,000 packages; 1915, 170,000, and 1916 the unusual amount of 229,000. There are two crops, the Bisakke or spring crop being the largest and producing the greater part of the T.N. grade. The fine orange grades are mostly derived from the Koosmie or fall crop, and being shipped during the winter, arrive in good condition.

Refuse lac. This is the residue left in the bag after the squeezing-out of shellac, as described above. It contains from 30 to 50 per cent sand and insoluble matter. The resin is soluble in alcohol or dilute soda, and is sometimes extracted. The lac may be precipitated from the soda solution by the addition of acid. The alcohol may be recovered by distillation, and the fused residue run out on a table or metal slab for the production of *garnet* shellac. In the pure form it is rosin-free; in the ordinary form it contains from 8 to 10 per cent rosin. It is marked A.C. garnet. The color is dark purple-red. Other grades are the Kala and Gal garnets, probably extracted with soda, which are almost black in color and contain 18 per cent rosin and upwards.

Button lac, when pure and of good color, is one of the highest-priced grades. It is characterized by its ready fusibility and ease of working when used for sealing-wax. It is prepared from special kinds of stick-lac of superior color in the same way as shellac, except that instead of being

drawn out in sheets it is allowed to harden in round disks two to three inches in diameter, which are stamped with the maker's seal, while soft. When held to the light, button lac is transparent and of a red-orange color.

Gross adulteration has been practiced in the past with button lac, rosin in amounts up to 40 per cent being not uncommon.

Constitution. Lac is a resin, but stands apart from the other resins in its origin and chemical characteristics. Tschirch, who has made the most thorough study of the chemistry of lac, classes it as an aliphatic or fatty resin, in which the substances of the fatty series predominate. His analysis of stick-lac is as follows: Wax 6.0 per cent, lac dye 6.5 per cent, resin 74.5 per cent, residue 9.5 per cent, water 3.5 per cent. The wax as shown by Benedikt consists of myricyl and ceryl alcohol, free and combined with various fatty acids. The resin may be divided into an ether soluble portion of 35 per cent and an ether insoluble portion of 65 per cent. The soluble part Tschirch finds to consist principally of fatty acids, a small portion of a wax-like substance, volatile with steam, and responsible for the characteristic odor of lac, a resin-like body (1.5 per cent of the raw material) and a yellow dye, erythrolaccin (about 1.0 per cent of the resin).

The ether insoluble portion of the lac resin is the resinotannol ester of aleuritinic acid. Nothing is known of the constitution of resinotannols. Tschirch considers the aleuritinic acid to be a fatty acid of approximately the constitution of dioxypalmitic acid.

The residue of 9.5 per cent consists of sand, wood, insect cells, etc.

Other investigators have detected the presence of nitrogenous substances in lac of a glutinous character (Hatchett, Gascard). A small quantity of sugar is shown by Fehling's solution in the aqueous extract.

Properties and Analysis of Shellac. Shellac is the form of lac commonly used in the arts, its flake-like form facilitating handling, and its large surface permitting the rapid action of solvents.

The specific gravity at 60/60° F. lies between 1.08 and 1.13. Accurate figures are out of the question, because shellac contains a large number of air-cells, as may be readily noticed when the flakes are closely examined.

The melting-point of shellac is indefinite. It commences to soften at 40° C., and gradually becomes more fluid as the temperature rises. It cannot be melted to a thin fluid without decomposition.

It is insoluble in acids, but readily soluble in alkalies, from which it may be recovered by neutralization. Mixed with water it dissolves in an eighth of its weight of sodium carbonate, when heated. It may be cut in borax, a convenient formula being 1 pound shellac, 4 ounces borax, 1 gallon water. Ammonia-water, triphosphate of soda, bicarbonate of soda may also be used as solvents. Caustic soda alters shellac chemically, converting it into a material only partly precipitated by acid. Lime water is not a solvent. From alkaline solutions shellac may be precipitated

by salting out, just as is done in the soap industry, a mass of a rubbery consistency being obtained.

Alkaline solutions of shellac have a strong purple-red color, due to the lac dye, which is never entirely removed by the washing of the stick-lac. They are also turbid, because of the insoluble, finely divided wax carried in suspension. The wax is sometimes removed by boiling the solution and skimming the melted wax from the surface.

Shellac is readily soluble in methyl and ethyl alcohol, as much as 10 pounds shellac dissolving in 1 gallon of the spirits. It is also soluble in fusel oil. Turpentine and benzine are not solvents, and will precipitate it from alcoholic solutions. Benzine is a solvent for shellac wax, however, and will remove it from alkaline solutions.

The iodine absorption of shellac is very low in distinction to the absorption of rosin, which is high. The measurement of the iodine absorption affords one of the best means of detecting adulteration. The purchase of shellac on analysis, with a guarantee as to rosin, has led to a great improvement in the quality of the shellac received at New York in late years. The absorption of iodine by the resins does not proceed to completion as with the fats, and it is necessary to lay down an empirical method requiring standard conditions as to time, temperature, and concentration. Using Wijs solution, and allowing it to act one hour at 22° C., it was found that high-grade shellacs, such as D.C. and V.S.O., absorbed from 14 to 17 per cent iodine. Good T.N. shellacs took 18 per cent. Rosin, while variable, averaged about 228 per cent. The method is based on the assumption that 18 and 228 are the iodine absorption numbers of rosin-free shellac and rosin respectively. Using these figures, the percent of rosin may be calculated from the iodine absorption. Results are undoubtedly somewhat below the truth, but the trade has become adjusted to these standards, and disagreements are rare. See reference at the end of this article.

Crude sugar has been used as an adulterant on T.N. grades in amounts ranging from 2–7 per cent. It can be easily detected by extraction of the pulverized shellac with water, evaporating on the water-bath and weighing the residue. After inversion a test may be made with Fehling's solution, bearing in mind that all shellacs contain a small amount of sugar.

The water extract in pure shellac should not exceed 0.3 per cent.

The insoluble residue left after extraction of the shellac with hot 95 per cent alcohol affords a measure of the insoluble impurities present other than the wax (the shellac wax is soluble in hot alcohol). A good T.N. should not contain over 3 per cent and a good orange mark not over 2 per cent.

Shellac is permanent in this climate, samples over 20 years of age showing no deterioration or change in chemical constants.

Bleached Shellac is prepared from shellac, seed-lac or stick-lac, by the

action of hypochlorite of soda on the alkaline solution, for the purpose of removing the red-brown color of the lac. The lac dye is bleached very quickly, but the yellow color of the erythrolaccin is more persistent and a greater or smaller quantity survives the bleaching entirely.

Shellac is *not* bleached commercially by the action of sunlight on the alcoholic solution, mixed with animal charcoal, by pouring the alcoholic solution into potassium hypochlorite, by boiling with weak potash, or by passing chlorine gas into the potash solution of the shellac, to mention a few of the methods permanently intrenched in the literature.

The only published method of practical utility is the following, from the *Papier Zeitung*, Berlin, Jan. 16, 1898: "Dissolve 1.6 kg. of soda in 50 to 70 liters of water, and heat to boiling. Add slowly 10 kg. of shellac. Make a solution of chloride of lime by adding to water in the proportion of 10 kg. to 200 liters. Run off the clear liquor and throw out the lime with soda. To the hot shellac solution add the sodium hypochlorite prepared as above until the color is wine-yellow. Add in small portions toward the end, waiting five minutes between additions. Cover and stand for several hours. Decant, warm to 30° C., and precipitate the shellac with hydrochloric or sulphuric acid, diluted to 1 to 20. Throw the bleached shellac into hot water and pull into bars.

Bleached shellac is sold in the form of pulled hanks or bars, resembling pulled sugar-candy in color and lustre. When the hanks are crushed and pulverized the bleached shellac is known as ground bleached. Both these forms contain about 25 per cent water. Formerly most of the bleached shellac sold was in the form of hanks, but of late years a steadily increasing amount of bleached shellac goes into the form of bone-dry bleached shellac, which is immediately available for the preparation of shellac varnish. Bone-dry is prepared from the ground bleached by treatment in a vacuum dryer or exposure to air on drying-frames until dry. It still contains several per cent of water. It is usually sold in barrels of 250 pounds net. Difficulty is experienced here with blocking in torrid summer weather, as noted in the case of orange shellac. To prevent this, bleached shellac should be stored in as cool a place as possible.

A peculiarity of bleached shellac is its gradual change into a modification insoluble in alcohol and alkalies. If not too bad the insoluble portions may be strained out of the solution, as the soluble portion is still perfectly good. This change cannot be prevented, and will inevitably take place in time with every bleached shellac. It is favored by high temperatures. Bleached shellac should be used promptly.

Bleached shellac dissolves in the same solvents as orange shellac. The solution is a milky-white, the milkiness being due to the presence of the insoluble shellac wax in suspension. In alcoholic shellac solutions the wax partly settles in time, leaving a clear light-yellow supernatant liquid.

Moisture in bleached shellac should be determined by drying to constant weight in a vacuo over sulphuric acid or by heating in a well-ven-

tilated air-bath at a temperature not exceeding 110° F., to prevent the sintering of the shellac. Heating at 50° C. and over results in the loss of volatile ingredients not water and a change in the chemical constitution of the shellac.

Refined Bleached Shellac. This is a wax-free form of bleached shellac, which dissolves to a clear solution in solvents. It is sold in the form of ground, hanks, and bone-dry.

Shellac Varnishes. These are often called simply "shellacs," the dry resin being incorrectly distinguished as "gum-shellac."

The bulk of the shellac varnish to-day is made with special denatured alcohol, a pure grain-alcohol denatured by the addition of 5 per cent wood-alcohol. The standard shellac is 5 pounds to the gallon, and is generally thinned down before use with wood-alcohol, the use of special denatured alcohol being not permitted. Orange-shellac varnishes are used where color is no objection, white shellac varnishes otherwise.

The alcohol is measured, and the weighed shellac added, without stirring or the application of heat. It is allowed to stand over night, and the next morning can be stirred with a stick until completely cut. If stirred too soon the shellac is apt to gather into a ball, which resists solution tenaciously. The yellow-colored residue sometimes noticed in orange-shellac varnish is a deposit of sand mixed with a little orpiment present in the original shellac, and insoluble in the alcohol. Water added to shellac varnish precipitates the shellac, but shellac itself may be cut in 85 per cent alcohol without difficulty. The addition of benzine or turpentine to shellac varnish will curdle the goods, and many complaints by painters may be traced to the use of these solvents as thinners or brush-cleansers.

Shellac varnishes are quick driers, the solvent evaporating entirely, and leaving the dry resin as a thin coating. This is in distinction to the oil varnishes, the solvent in this case forming an integral part of the dry coat. Special denatured shellac varnish dries somewhat more slowly than the wood-alcohol varnish, but the end-product is the same. The alcohol in evaporating chills its surroundings and attracts water from the air, especially in humid summer weather. This produces a whitish film, which slowly disappears.

Shellac varnish is rather extensively adulterated. Spirit-soluble resins, such as rosin, copal, and sandarac are used. Celluloid is sometimes added to give a fictitious body. Foreign resins are easily recognized by a colorimetric test with dilute Wijs solution. The body may be determined by evaporation.

French Varnishes and Lacquers. A French varnish is a transparent shellac varnish and may be made either by the solution of refined shellac (wax free) in alcohol, or by the filtration of shellac varnish to remove the wax. In some cases French varnishes are made from copal and sandarac.

Colored lackers are made by the solution of the appropriate color in the French varnish.

Uses and Applications. Shellac is used as a binder in composition goods, such as buttons, dominoes, poker chips, telephone receivers, phonograph records; in the electrical industry as an insulator; in sealing-wax, etc. Cut in alkalies it serves as a dressing on leather and patent leather, shoe polishes, as a finish on playing-cards, surface-coated papers, and hats. Dissolved in alcohol it is very extensively used as a quick-drying varnish on all kinds of furniture, interior decorations, railroad and trolley cars, hat stiffening, kalsomining, pencils, brewers' varnish, patterns, parquet floors, etc.

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CHAPTER XXXV

RUBBER AND RELATED GUMS

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Botany. Plant investigators have known for a long time that certain plants are characterized by the presence of capillary vessels containing a milk-juice. This latex, as it is called in the Tropics, is found in the stems, leaves, bark and roots of various trees, shrubs and creepers. This milk-juice is in most cases secured by making incisions on the trunk of the tree in such a manner as to sever the milk bearing canals. The milk at once exudes and is collected in tins of about $\frac{1}{2}$-pint capacity. It is then coagulated or cured by exposure to smoke, or by treatment with organic acids. We are at present acquainted with about twenty genera of these plants belonging to the following families (according to Strassburger): Euphorbiaceæ, Apocynaceæ, Moraceæ, Compositæ, Convulvulaceæ, Asclepiadaceæ. The latex is apparently an emulsion containing generally five substances, present in varying proportions, depending upon the source of the latex. Two specimens showed on analysis (in round numbers):

	Hevea Brasiliensis	*Funtumia Elastica*
Water	55.0%	50.5%
Rubber	38.5	40.7
Proteins	3.0	3.3
Resins	3.0	4.5
Mineral matter	0.5	1.0

Definitions. Rubber is a hydrocarbon contained in the latex of certain milk-bearing plants found principally in the Tropic zone. The rubber of commerce known as "washed and dried rubber" contains in addition to this all the substances enumerated in the above analysis, in varying proportions. The trade names of some varieties of rubber are: Para from Hevea species; Caucho (Amazonian and Mexican) from Castilloa; Mangabeira from Hancornia; Manicoba (or Ceara) from Manihot; Assam from Ficus; African from Landolphia and Funtumia. Plantation rubber from the Middle East is obtained principally from Hevea Brasiliensis. The question of terminology was discussed at some length at the International Rubber Conference held in New York City in 1912 Many careful men

in the rubber trade now speak of "Hevea rubber from Ceylon" and "Hevea rubber from Para" but rubber brokers are as a rule opposed to such discrimination. The terms "Up river Fine Para" "Caoutchouc" and "India rubber" are still seen in badly drawn specifications. They are remnants of the time when nearly the whole world production of rubber was shipped from Para and the Indies. The English term "Fine hard Para" is equivalent to the American term "Up river fine Para."

Although it may be said of nearly all products of the animal and vegetable kingdoms, that they are difficult to define, this is more especially true of rubber, in fact it was not until 1905 that a definite knowledge of the actual rubber substance was obtained. For over fifty years, it was defined merely as a hydrocarbon having the empirical formula $C_{10}H_{16}$, but in 1905 Harries of Kiel defined it as a highly polymerized 1-5-dimethyl-cyclo-octadien-1-5. Oxygen in the form of ozone reacts very readily with this substance, forming various "ozonides." It has also been observed that oxygen has a detrimental influence on rubber and rubber products, so that we may conclude that the closer rubber approaches to the chemical formula mentioned, the more desirable it is for most purposes. Nitrous acid reacts with rubber to form "Nitrosites." If rubber is heated in the open air to 285° C. it loses all its natural elasticity and assumes the condition of a liquid which remains fluid at ordinary room temperature.

Chemical and Physical Properties. The chemical properties which give rubber its commercial value are its resin content, and its reaction with elemental sulphur. Good Hevea rubber contains seldom more than 3 per cent of resins while soft Guayule rubber may contain as high as 20 per cent of resins. These are soluble in aceton, and this solvent is used on a large scale for deresinating rubbers which contain excessive amounts of resin. Volatile organic solvents such as turpentine, carbon tetrachloride, coal-tar benzol and petroleum benzine cause rubber to swell to a jelly-like mass. This mixture becomes distinctly viscous on further dilution, in fact Fol of Delft has endeavored by numerous experiments to show the relation between viscosity, resin content and strength in "washed and dried" rubber. The most important chemical property is without doubt the fact that rubber combines with sulphur in all proportions, the highest being a product containing about 32 per cent of sulphur. This chemical combination of rubber with sulphur is known in practice as "vulcanization."

The physical properties which give rubber its value as a material of commerce are: (1) pale color; (2) high tensile strength when compounded; (3) high adhesion and cohesion values; (4) great elasticity; (5) pliability within a great range of temperatures; (6) impermeability to water and gases; (7) enormous dielectric value; (8) ability to "take up" powdered minerals and form with them a homogeneous mass or dough; (9) specific gravity, less than that of water.

Geography. Rubber-producing plants are found in the forests along the Amazon River in Brazil. The names of its tributaries are, in fact,

used in the trade to designate particular grades of rubber. For example: Javary, Jurua, Purus, Tapajos, Xingu, and Madeira. The width of the Amazon basin is given as " 5 to 15 miles," and its length as " over 3000 miles," from which we may form some idea of the vastness of the Amazonian jungles. Other rubber-producing countries are Africa, Mexico, Central America, East and West India, and last, but not least, the Middle East, where Plantation rubber has been cultivated since 1876. The term " Middle East " is used to designate that part of the Tropics at about 100° East longitude. It includes Ceylon and Malaya.

Commerce. Since the year 1913 over half of the world-production of rubber has been obtained from plantations. The Malay States alone produced in that year over 25,000 tons of washed and dried rubber. In January, 1917, the New York price of rubber was quoted at 78 cents per pound for " Up river Fine Para "; 78 cents for " first latex pale crepe " plantation rubber; and 80 cents for " Smoked ribbed sheets " plantation rubber. Para rubber is put on the market in " Biscuits " (pelles, or hams) resembling large watermelons, which lose about 20 per cent of their weight on washing and drying. They are called " hams " because of the peculiar smoke odor which clings to the rubber from the smoking, or curing operation. Some grades of African rubber lose as much as 50 per cent of their weight during washing and drying.

The rubber-goods factories of the United States have for a number of years required over 50 per cent of the total world production of rubber. The approximate production of tons of rubber in the world is given in the table. It should be noted that 1 ton of rubber weighs 2240 lbs. Avoir. The figures for " all wild rubbers on a washed and dried basis " were obtained by allowing a 25 per cent shrinkage on the total wild rubber production of the world. This is considered preferable to the usual form of statistics wherein " wild, crude rubber " is compared directly with " washed and dried rubber " production.

WORLD RUBBER PRODUCTION

	Rubber from All Plantations.	Wild Rubber from South America.	Wild Rubber from all Other Countries.	All Wild Rubber on Washed and Dried Basis.	World Rubber Production on Washed and Dried Basis.
1912	28,500	40,500	29,500	52,500	81,000
1913	47,200	40,000	21,400	46,050	93,250
1914	65,000	37,000	18,900	41,925	106,925
1915	100,000	37,500	15,100	39,450	132,850
1916	152,000	37,500			
1917	200,000	37,500			

Materials

Crude Rubber from Plantations. This material appears on the market in two principal forms. " Smoked sheet " is produced in the Middle East by coagulation of the latex and smoking in specially constructed apparatus.

In Wickham's machine the fresh milk-juice is poured into a revolving drum, and is thus made to spread a fine coating of rubber. The drum revolves in a chamber, filled with wood-smoke. The best apparatus now available produces not more than 15 lbs. of dry rubber per day, a rate of production entirely too low to warrant extensive use. The method more commonly used for producing "smoked sheet" is to convert the coagulated lumps of rubber into sheet form and then hang these sheets in a "smoke-house" at about 100° F. for twelve hours. Early observers claimed that the "curing" of rubber in Para was effected chiefly by the creosotic contents of the smoke, but Sidney Morgan, a plantation-rubber specialist, is of the opinion that the "cure" is effected chiefly by heat and such smoke constituents as formaldehyde. The creosote *does* apparently prevent the formation of mildew on the rubber.

Brazilian plantations are now in operation in the district of Bahia, 800 miles south of the equator, and the rubber (*Hancornia* species) appears to possess many good qualities. In Acre, Brazil, many hundred thousand trees have been planted, so that these will soon add to the world's production of rubber.

Plantation rubber from the Middle East is obtained principally from *Hevea Braziliensis.* This is botanically the same as the wild rubber tree which grows near Para in Brazil. Hence, some have fallen into the error of calling this product "Plantation Para." Others use the term "Ceylon crêpe" for all rubber which comes from plantations in the form of crêpe or thin sheets. Both these terms are incorrect and they do an injustice to the Plantation Industry which has been so successfully fathered by the English colonials in Ceylon and Malaya.

South America to-day offers to investors unusual opportunities for plantation development. The Government of Brazil has of course been active in the matter, and has passed laws which encourage the planting of trees and the export of the product. Large operations in that country should, however, be preceded by the establishment of American Bank-agencies, as the local banks are not in a position to finance the plantations without such assistance. In view of this it seems most logical that American banks should lend assistance to an industry which is undeveloped chiefly for lack of funds. If this financial aid is refused by America, the foreign investment companies will no doubt soon realize the advantages of the situation.

Plantation rubber has been purchased with hesitation by the smaller manufacturers, as they are not prepared to do much experimental work. The commercial grades yield different results when compounded, and these variations can be traced to: (1) the chemical composition of the rubber; (2) the age of the tree from which the rubber was obtained; (3) the manner of collecting and coagulating the latex. It is conceded that one method of coagulation will not serve for all varieties of latex. Hence, it is important that the ultimate consumer know the methods used on

the rubbers which he buys, so that this may be taken into consideration when the gum is compounded in the factory.

The market value of crude rubber is influenced by many factors, among which are: (1) *Tackiness*, especially noticeable in soft Guayule rubber containing much resin. (2) *Acidity*, found chiefly in acid-coagulated plantation rubber. (3) *Softness*, in poorly cured Para rubber and African rubbers. (4) *Cleanness*, in cases where the rubber is sold in the washed and dried condition. (5) *The proportion of unsmoked* or poorly smoked latex in the "pelles" or Para rubber. (6) *Toughness*. (7) *The age of the "pelle,"*—fresh pelles contain more moisture than those which have been stored for some months. (8) *Color*—pale rubber is for some unknown reason uniformly preferred by buyers. (9) *Tensile strength*—this is determined by mixing up the rubbers on a "standard recipe" and then comparing the tensile strength of the cured compounds. (10) *Stretch*, is determined by observing the extent to which a strip of vulcanized rubber compound can be stretched without rupturing it.

Reclaimed Rubber. This material occurs in commerce in many grades, varying in price from 10 to 50 cents per pound. It is known as reformed, recovered, or regenerated rubber. The colors usually found are red, white, and black. Commercial samples of high-grade "floating stock" and a low-grade stock, "heavier than water," showed on analysis (*in round numbers*):

	Floating.	Heavy.
Rubber	90.00	57.00
Aceton-soluble matter	4.00	10.00
Mineral matter	2.95	30.45
Combined sulphur	3.00	2.50
Free sulphur	0.05	0.05
Specific gravity	1.00	1.17

The reclaimed rubber offered to rubber-goods manufacturers is frequently designated according to its origin, as "gum-shoe stock," "tire-tread stock," "airbrake-hose stock," etc. The processes of reclaiming may be considered under three groups: (1) the removal of textile fibers; (2) the removal of sulphur; (3) the removal of mineral matter. The separation of cotton fiber from scrap rubber can be effected by the *Flotation method*. In this case the shredded scrap is subjected to fractionation by means of an air blast. The heavier particles (the rubber compound) are left behind while the fiber is blown off. The most advanced procedure is that known as the *Mitchell method* (U. S. P. No. 395,987, issued in 1889 to J. K. Mitchell of Philadelphia). According to this process, the waste rubber is immersed in an acid solution in a sealed vessel and subjected to pressure above the boiling-point, in fact 240° F. until the material is corroded and removable by washing, after which the waste is steamed at

high pressure to effect devulcanization. The removal of sulphur from scrap rubber is best accomplished by means of the *Marks alkali method.* This is covered by U. S. Patent No. 635,141 granted to Arthur Marks in 1899. This consists in subjecting the ground rubber waste, when submerged in a dilute alkaline solution (for example a 3 per cent solution of caustic soda) to the action of heat, say from 344 to 370° F. for twenty hours, under conditions which prevent the evaporation of any considerable quantity of the solution. It is claimed for the process that it so removes vegetable fiber and sulphur from vulcanized rubber, that when the product of the process is thoroughly washed to remove the chemicals there remains devulcanized rubber having substantially the characteristics of fresh rubber and capable of being used in like manner. In this process the caustic soda acts directly on the sulphur, and the rubber is softened. Another process used for the removal of free sulphur from scrap rubber is known as the "*Oil method.*" In this case the ground rubber scrap is mixed with rosin oil or with plant oils and this mixture is placed in autoclaves at high temperatures. The sulphur of the rubber compound is attracted by the oil, the oil is sulphurized and the final result is a plastic product which can be added to fresh rubber compounds and revulcanized. For the removal of the mineral matter from old rubber goods it has been proposed to use the Centrifugal method. In this case the ground is treated with gasolene, benzol or other light solvent and the whole mass is placed in a centrifugal separator. Reclaimed rubber is frequently preferred by manufacturers to other organic fillers, because it does actually contain more or less rubber, even though this rubber content may be low. Skilled buyers of this material usually calculate its value in a way similar to the following:

"If a 100-pound lot of reclaimed rubber contains 50 ponnds actual rubber, and 50 pounds substances not rubber (average value 2 cents per pound), what does this rubber-substance cost me?" If fairly good rubber can be bought at 50 cents per pound, this rubber-content would have, *at most*, a value of 50 pounds$\times$50 cents$=$\$25. Hence, such a reclaimed rubber should not cost the consumer much above 25 cents per pound. This simple problem in calculation some consumers seem to have overlooked.

Aside from the chemical tests indicated in the analysis shown above the buyer lays great stress on the results of the tensile strength test and the "Permanent set after elongation." The U. S. Court of Customs Appeals in 1911 decided that reclaimed rubber is *not* a manufactured article.

Organic Fillers. This group of compounding materials includes a great variety of substances which are valued because they possess a certain cohesiveness and they combine readily with most other fillers. Materials containing more than 0.5 or 1.0 per cent of moisture or "matter volatile at 150° C." are generally barred from use. (1) Brown substitute is made

by heating certain vegetable oils with powdered sulphur at higher temperatures. (2) White substitute is made by treating vegetable oils with dilute solutions of sulphur chloride. These oil substitutes are useful in compounding stock which is to be forced through a tubing machine. White floating substitute is a carefully prepared variety, valued because of its low specific gravity. The analysis of these substitutes includes a determination of: Ash, moisture, free sulphur, organic aceton soluble matter. (3) Pitch hydrocarbons include the pitch residue obtained from coal tar, the blown-pitch residue obtained in petroleum distillation, and the stearin pitch obtained as a side product in the manufacture of stearic acid. It should be remembered that coal-tar pitch contains mostly saturated hydrocarbons, petroleum pitch contains mostly unsaturated hydrocarbons and stearin pitch contains more or less saponifiable matter which is capable of uniting with sulphur at high temperatures. "Kapak" is a valuable hydrocarbon prepared from Gilsonite and Elaterite and asphaltum. (4) Vegetable oils and waxes. (5) Animal fats and waxes. (6) Mineral fats and waxes including vaseline and paraffin. (7) The glue-tannin compound softened with glycerol is extensively used as an addition to rubber compounds.

Mineral Fillers. This group of compounding ingredients includes: (1) Accelerating agents—substances which hasten the "cure." (2) Strengthening agents—substances which increase the tensile strength and decrease the extreme elasticity of rubber. (3) Weighting agents—substances which are added more especially to reduce the "price per pound" of the finished product. (4) Coloring agents. (5) Abrasive agents—for erasers. (6) Dehydrating agents which prevent the formation of blisters during vulcanization. (7) Vulcanizing agents: sulphur is the essential ingredient of all rubber mixings which are to be vulcanized.

Commercial antimony penta-sulphide, known in the trade as crimson antimony, usually contains from 15 to 17 per cent of free sulphur, and the vulcanizing power of that material is undoubtedly due to this fact. Antimony penta-sulphide also acts as a carrier of sulphur, so that rubber may be vulcanized by using it in conjunction with smaller quantities of sulphur than would otherwise be needed. Goods containing sulphide of antimony will be colored red, but not all rubber-goods which are red contain it. In recent years red oxide of iron and insoluble organic colors have been used as substitutes for the red color of the expensive antimony compound.

Litharge and magnesia are usually classed as sulphur "carriers," as it has been observed that compounds containing these materials vulcanize more readily than those which do not. Rubber products containing litharge or any other lead compound will be colored black, hence the analyst concludes at once that white and light-colored products do not contain any lead. Barytes, lithopone, zinc oxide, whiting, gypsum, magnesium carbonate, asbestos, silica, natural silicates, belong to a group of mate-

rials which are useful in the production of white rubber-goods. They incidentally add body and rigidity to the product, and enable the manufacturer to sell his goods at a fair price.

A considerable part of the whiting used in rubber-goods manufacture is known in the trade as " water-floated." In this process the crude chalk mined in England and France is mixed with water in large tanks in such a manner that the heavy particles of flint have an opportunity to settle to the bottom of the tank. By arranging these settling-boxes ten or fifteen in a series it is possible to obtain a product quite free from this contamination. The whiting so produced can be bolted through a " 200-mesh " wire screen without difficulty.

Graphite, used to a large extent in steam packings, is prepared on an industrial scale by " air-flotation." In this process the heavy particles containing alumina, silica and iron sink to the floor of the chamber while the lighter particles of graphite are blown to the farther end of the compartment by means of a current of air. In the preparation of this material the method of " water-flotation " is obviously impossible, as the graphite has a distinct water-repellent property.

It seems necessary to correct the presumption that all these materials are adulterants. The tremendous elasticity of pure rubber compounds would be of little value to the user of airbrake-hose, rubber mats, and hot-water bottles. And it is chiefly for this reason that the manufacturer is constantly on the lookout for materials which will counteract this excessive elasticity and incidentally increase the tensile strength of the finished compound. This interdependence of " strength " and " stretch " in rubber-goods is a fact which cannot be ignored in the rational compounding of rubber.

The coloring matters at the disposal of the rubber chemist are few in number, owing to the impossibly high prices of the brilliant pigments. The principal coloring materials now in use are: vermilion, antimony sulphide, red oxide of iron, ultramarine, lampblack, chrome yellow, burnt umber, and burnt sienna. Certain lakes of organic dyes have also been used successfully for coloring rubber compounds.

Proteid Fillers. The use of animal glue as a valuable addition to rubber compounds has been known since about the year 1910. For this purpose glue paste is treated with cresol, or tannin, or formaldehyde or bichromates. Valuable products are also obtained by using two or more of these materials in conjunction with the glue.

Solvents. Organic solvents used in the rubber industry are few in number. In the " cold cure process " the sulphur chloride is dissolved in carbon tetrachloride or in benzol. For the preparation of cements, a petroleum naphtha of 85° Bé. is used. For washing the iron cores of rubber-covered rolls to aid the adhesion of the rubber compound to the iron, a highly volatile solvent is preferred. Naphtha of 85° Bé. and pure benzol have been used for this purpose. For the removal of resins from low-

grade rubbers, the material is extracted in special apparatus with aceton. Since the opening of the war in Europe, a series of oils known as " ketone solvent " have found successful application in resin extraction. They are obtained from the distillation of hard woods and are designated as No. 1 Solvent (B. P. under 100° C.), No. 2 Solvent (B. P. under 150° C.), and No. 3 Solvent (B. P. under 200° C.).

At this point mention should also be made of the crude carbolic acid, pine oils and rosin oils used in the reclaiming of rubber by the oil process.

Textiles. The textile materials used in the rubber industry include: (1) The cotton yarn used in the manufacture of jackets for cotton-rubber-lined hose; (2) hose duck, used for the manufacture of hose for conveying steam, water and air; (3) belting duck, used in the construction of belting for conveying ores and belting for power transmission; (4) auto tire duck, used for building the body of automobile tires; (5) packing duck, used in the construction of such products as " Manhattan, rock-hard, hydraulic piston packing."

Asbestos fiber has been used very successfully in the manufacture of high-pressure packings used in modern steam turbines. These are knows an asbestos-rubber packings and are marketed under such names as " Tauril " and " Durabla." Heavy asbestos fabric interwoven with fine copper wire has been used for some time in the manufacture of " brake band linings " for automobiles.

Processes.

The operations of the rubber industry may be grouped into: (1) Preliminary processes, including coagulating the latex, washing. (2) Principal processes, including mixing, calendering, vulcanizing. (3) Special, such as extrusion of tubing for auto inner tubes; cutting tubing on the lathe, for jar-rings; vulcanizing semi-cured tubes in the fire hose jacket; manufacture of automobile tires.

Coagulation. The principal methods used for coagulation are:

1. The use of heat and smoke. This is the chief method used in the Amazon valley where the latex is exposed over a fire.

2. Heating the undiluted latex.

3. Diluting the latex and adding chemical solutions in the cold. The chemicals used in Brazil are alum and phenol, while acetic acid and tartaric acid are used on the plantations of the Middle East.

4. Placing the diluted latex in a centrifuge. The rubber is separated from the water in a way similar to that observed in the " cream separator."

Method No. 1 deserves special mention. It has been adjusted to meet modern requirements by J. A. Da Costa of Para, Brazil, and Robert Bridge of Manchester, England. This process consists in the injection of wood-smoke into the latex by means of steam, at a comparatively low pressure. Coagulation is effected by the volatile acids and creosote in the smoke, so that many gallons of latex can be treated in a few minutes,

and the rubber is removed completely from the water. The method closely approaches that used originally by the natives of Brazil. The product is far superior to that obtained by the various methods of coagulation with chemical solutions.

Washing. The first operation which is carried out at the rubber-goods factory is the washing of the crude rubber. Figs. 330 and 331 repre-

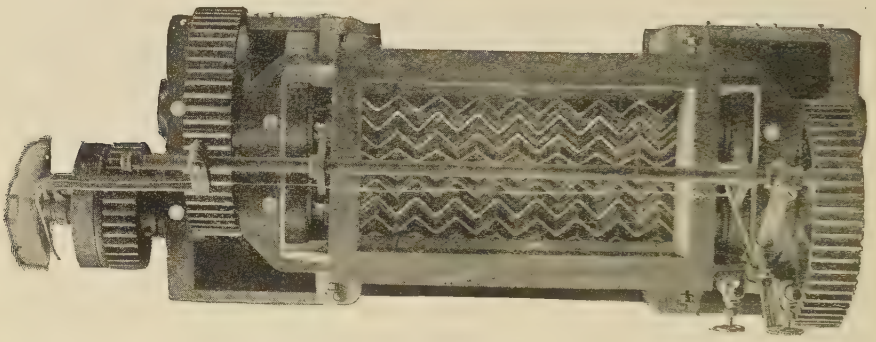

FIG. 330.

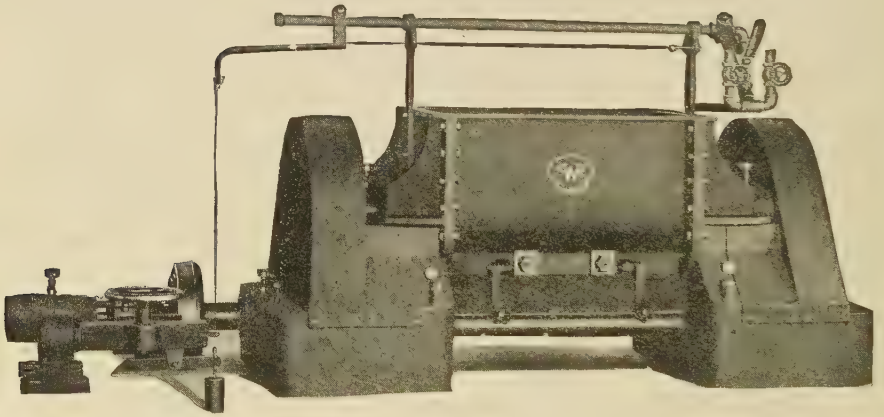

FIG. 331.

sent a top and side view of the Werner–Pfleiderer rubber washer employed for the purpose of removing bark and wood and water-soluble impurities from the rubber. It seems almost as if, even this operation would be eliminated from the factory as the plantation rubbers are now put on the market in the washed and dried condition, and many manufacturers are beginning to discontinue the use of the wild *unwashed* rubbers. This is a most desirable state of affairs, as the operations of

washing and drying rubber can be conducted with advantage directly at the primary markets. Moreover the transportation of 20 to 40 per cent of worthless foreign matter is rather irrational.

No doubt the Brazilians will soon realize the advantages to be gained by carrying out these operations near the source of production, just as is now being done in Malaya and Ceylon. The washing operation consists in passing the crude material over and over again between corrugated rolls while it is being sprayed by a series of fine streams of water. Rolls grooved in the form of a diamond are now generally preferred, especially in those cases where the sheets are to be transported some distance. The deep ridges in this case allow of a free circulation of air, and thus prevent the formation of mildew. For use in the factory, it is suggested that a battery of two machines be used. The first to have " rough-cut " rolls, the second to have " medium-rough " surfaces. A convenient size of rolls is 18 ins. diameter, and 30 ins. long. They may be driven by individual electric motors, and geared to a differential speed of six revolutions (back roll) to five revolutions (front roll).

A modern type of washing machine, Figs. 330 and 331, is especially well adapted to the washing of scrap rubber is that known as the W. and P. Universal. The arrangement of the rollers and the shape of the machine is such as to allow the washing to be done with the minimum pressure on the rubber. At the same time the sand and bark are discharged automatically as they leave the rubber. The product is in the form of rather thick pieces which must be crêped before drying. In such a machine 300 pounds of dirty African rubber can be washed in one-half hour, using 20-horse-power. The machine requires little attention from the workman.

Drying. The operation of drying is most necessary, as moist rubber can under no circumstances be used for rubber mixings. If the material were to be put on the mixing rolls immediately after washing, much time would be consumed in heating the rolls and the rubber to a temperature which would insure the expulsion of the water. For this very simple reason the manufacturer in his factory, or the grower on the plantation, dries his product. In the early days of the industry, rubber was hung up to dry for a period of six months, and the drying was done in special " lofts " through which a current of dry, warm air was passed. Manufacturers in America have replaced this time-consuming method by more modern drying process. Those who have refused to adopt this method for mechanical rubber-goods may well be said to have dropped out of the procession. On the other hand it is generally admitted that rubber for *pure gum* articles, elastic thread, and elastic bands should be dried by the older process. The modern vacuum dryer, Figs. 21 and 22, has made it possible for the manufacturer to use the rubber twenty-four hours after it has been washed—in fact, it may be taken directly out of the drying chamber and put on the mixing mill, thus avoiding the necessity of " breaking-down " the rubber. In the

vacuum dryer the washed rubber is laid in pans after it has been sprinkled with talcum powder (soapstone). An apparatus which will dry 2 tons of rubber in ten hours occupies a space $9' \times 9' \times 15'$.

Breaking down, in the majority of cases immediately precedes the mixing operations on the same machines. It is done for the purpose of rendering the rubber plastic and eliminating the innumerable air spaces which are noticed in the rubber as it emerges from the vacuum dryer, or from the old-style drying room. In order to "break-down" the material it is run on the rolls until it has become quite warm. In the case of Para rubber, a rather high temperature is required, and even then some time is consumed before this is accomplished. For this reason hard, fine Para rubber is sometimes broken-down by the consumer in advance of the time when it is to be mixed. After this operation the rubber appears in sheets 1 inch or $1\frac{1}{2}$ inches thick, with a rather smooth, shiny surface. It may then be put aside for any length of time until required.

Mixing. The mixing operation has for its purpose, primarily the admixture of some vulcanizing agent with the rubber. This then is the

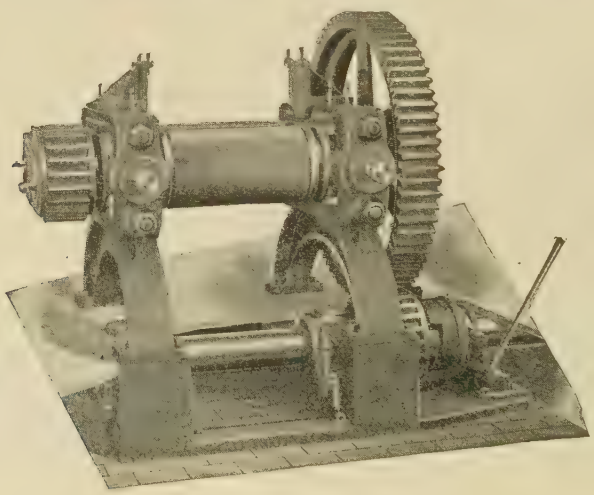

FIG. 332.—Farrel Rubber Mixing Mill.

simplest form of rubber mixing which can be produced. A glance at the interior of a rubber factory, or a look at a garden hose which has passed through an intense fire tell, us, however, that there are other materials besides rubber used in rubber mixings. These materials have been reviewed previously under "Materials" as Organic Fillers and Mineral Fillers.

The mixing mill, Fig. 332, consists essentially of two hollow steel rolls revolving against each other. The front roll makes approximately 16 revolutions per minute while the rear one makes 24. Suitable appli-

ances make it possible to lead either steam or cold water into each of the rolls. This is most necessary when working very soft or very tough mixings. In the latter case, it is at times difficult to maintain the whole mixture in a state of plasticity, and then the operator can resort to steam for heating the rolls. As a result of the uneven speeds at which the front and the rear rolls revolve, the compound usually clings to the slower-moving " front " roll (the one nearest to the operator). If, however, the mix becomes very hot or the rolls are pressed too close together the compound will wrap around the back roll. In order then to bring it back to the front roll, the operator turns cold water into the rear roll and loosens the set screws which serve to jam the rolls together. It is important to note that the mixing operation must not be unduly prolonged, and for this reason the operator must use every minute of his time to advantage when there is a " batch " on the rolls. If, for any reason, he has lagged, this will soon be apparent in the consistency of the mixture. It becomes very hot and sticky and it is difficult to remove it from the rolls by the usual method of cutting off with a knife. A far more important result of this overworking is the defect known as " fatigue." This being interpreted means that the rubber loses much of its rubbery quality, its " nerve," and when the vulcanized product is tested for tensile strength and " stretch," abnormally low figures are obtained. A skilled mixer must be able to produce a homogeneous mixture of the rubber and the fillers, with a minimum loss of material, in a reasonable time. This last term will vary with the character of the fillers which are used in the mixing. Thus magnesia and lampblack are very light and " fluffy," and for this reason are quite difficult to incorporate with the rubber. The " time " factor is influenced also by the speed of the mixing rolls, the size of the mixing rolls, and the total weight of the " batch " to be mixed. Immediately after being cut from the rolls the batch weighing anywhere from 25 to 100 pounds, is thrown on the table in the batch storage room and is there sprinkled liberally with soapstone in order to prevent sticking to the table. If it is to be used at once it is transferred directly to the calender, while it is still hot.

Calendering. The purpose of calendering the rubber " dough " or " batch " is to produce sheets of uniform thickness, which can be vulcanized for steam packings, or for building up articles of greater thickness. The machine, Fig. 333, in almost all cases consists of three rolls placed vertically one above the other. If these be designated as No. 1, beginning at the uppermost roll, we note that No. 1 and No. 3 revolve " clockwise " while No. 2 revolves anti-clockwise. The warmed rubber dough (or compound) is fed in between rolls No. 1 and No. 2. It then passes around roll No. 2 and finally between roll No. 2 and roll No. 3. As it emerges from these rolls is it led to a near-by winding roll which revolves anti-clockwise. A layer of muslin is wound between the layers of the sheeted rubber, while it is wound on the winding roll. This prevents the layers

from adhering to one another. Fabrics which are used in building up rubber belting, and automobile tires, have a thin layer of rubber compound applied to them on the "friction calender." In this case the calender is arranged so that roll No. 3 moves more slowly than roll No. 2. This differential speed causes the compound to be rubbed well into the fabric.

Vulcanizing. The object of vulcanization is to produce a chemical union of rubber with sulphur, and thus obtain a material which will possess strength and elasticity. It was first observed by Charles Goodyear, of New Haven, Conn., in 1839, and later independently recorded by Thomas

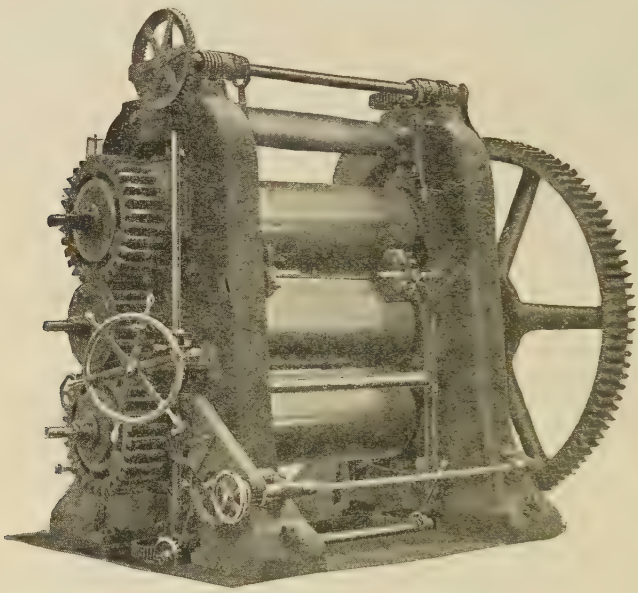

Fig. 333.—Farrel Rubber Calendar.

Hancock, of London, Eng., in 1843. These experimenters heated rubber with sulphur while the mass was under *pressure*, but Alexander Parkes, of Birmingham, Eng., showed in 1846 that thin layers of rubber may be vulcanized by immersing in a solution containing 2 or 3 cc. of sulphur chloride in 100 cc. of such volatile solvents as carbon disulphide, carbon tetrachloride, and benzol. The Goodyear method is known as the steam cure, and is carried out in an autoclave or in a press between plates. The Parkes method is known as the acid cure (or the cold cure), and is carried out by immersing the article in a tank containing the solution of sulphur chloride. The poisonous character of the gas makes it necessary to use a hood in connection with this "dipping" method. The process of vulcanizing or "curing" rubber-goods by Goodyear's method is influenced

by several factors, among which may be mentioned: (1) the rubber which has been used; (2) admixture of "catalytic" agents to the compound; (3) proportion of sulphur in the mixture; (4) the temperature at which the goods are "cured"; (5) the time or duration of the cure; (6) admixture of basic, or dehydrating agents to the compound. The methods of vulcanization in use at the present day vary according to the kind of goods to be treated. Thus automobile tires, air-brake hose, rubber belting, toy balloons, and rubber overshoes are each cured according to a special

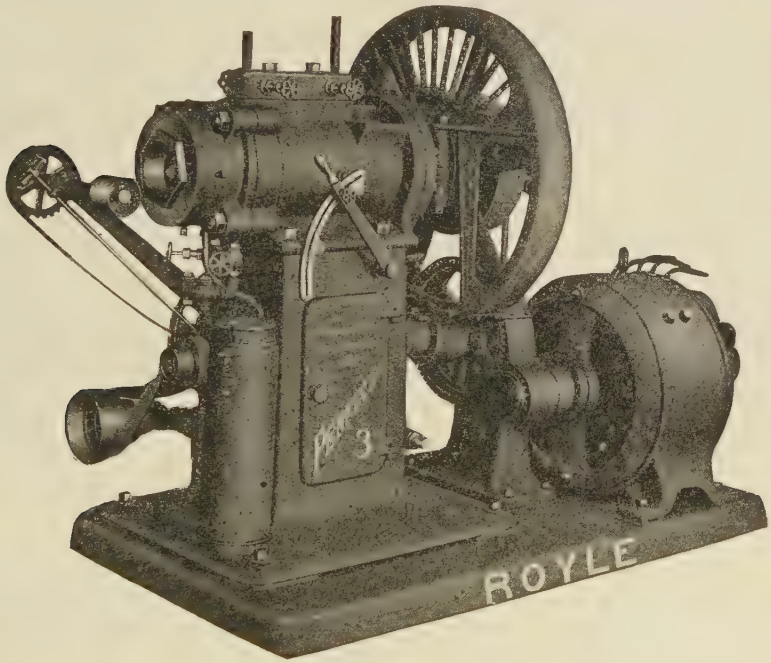

Fig. 334.—Tubing Machine.

method. These methods are known as: (1) steam cure, (2) dry heat cure, (3) press cure, (4) cold cure, (5) vacuum cure.

Manufacture of Rubber-covered Wire. In this process both wild "Para" rubber and cultivated "Hevea" rubber is used. The consumers of wire now recognize the fact that it is important to specify the chemical and physical properties which the product must possess. After washing and drying, the rubber is mixed with sulphur, and certain minerals and organic materials, such as zinc oxide, talc, whiting, litharge, barytes, white lead, paraffin wax, montan wax, ceresin, and ozokerite. Other materials used in the manufacture of insulated wire are: gutta-percha, balata, and coal-tar pitch. These materials are mixed with the rubber in the usual manner. The "dough" is then pressed on to the wire through dies, or it is applied in the form of a longitudinal

strip which is pressed around the wire in tubular form. Copper which is in direct contact with vulcanized rubber will suffer corrosion if there is an excess of sulphur in the compound. This in time will interfere with the insulating power of the covering, hence the copper wire is tinned, and wrapped with a thin layer of unvulcanized rubber before the final covering is put on.

In the "Seamless Method" insulating, the compound is forced, while in a soft state, through a hole in a tubing machine. The diameter of the hole is equal to the desired outside diameter of the insulation on the wire which is being made up. The compound is forced out of the machine by means of a hollow screw. Through the center of the screw the copper wire is fed forward at a predetermined rate of speed.

In the "Seam Method" thin sheets of rubber are passed though specially grooved rolls through the center of which the wire to be insulated runs. These sheets are pressed tightly around the wire, and locked together by means of a seam automatically formed by the rolls. The edges of the upper and lower sheets of rubber are folded into each other. Vulcanization is carried out by placing the covered wire in a chamber containing steam under pressure, or—heated air. The temperature in the vulcanizer varies from 120 to 150° C., and the duration of the treatment varies from one hour to two or three hours, depending upon the particular product which is being manufactured.

Products

Manufactured rubber-goods may be roughly divided into those containing textile fibers and those which do not contain this material. This is a distinction which would be made by a reclaimer of old rubber-goods, because of the fact that different methods of reclaiming must be applied in the two cases. In the first division we find automobile tires, garden hose, railroad hose, belting for power transmission and conveying door-mats, and fire hose.

In the second division we find the major portion of all druggists' sundries, erasers, elastic bands, dental gum, stamp gum, steam packings and laboratory tubing. Other rubber products are: rain-shoes, rain-coats, cements, "Ebonite" combs, bath sponges, insulated wire, thread for elastic webbings (suspenders and stocking garters), football bladders, toy balloons, syringes, soles and heels for shoes.

Ebonite, or hard rubber, is the term applied to the product obtained when rubber is mixed and vulcanized with high percentages of sulphur. In this case the compounder uses as much as 30 pounds of sulphur for each 100 pounds of rubber used in the recipe, while in the usual rubber mixings he would use from 5 to 7 pounds of sulphur for that much rubber. Investigation has shown that rubber is capable of combining chemically with varying amounts of sulphur, but this remarkable "power of accommodation" has not yet been satisfactorily explained.

The diagram, Fig. 335, has been prepared to show in a general way the conversion of latex into manufactured rubber-goods. The products mentioned above can be made out of the materials indicated, but it cannot be said that each article mentioned is always made out of all the materials shown. In the manufacture of all classes of rubber goods there is obtained a certain amount of "unvulcanized scrap." If this contains textiles it is reclaimed by destroying the vegetable fiber. If it contains no textiles

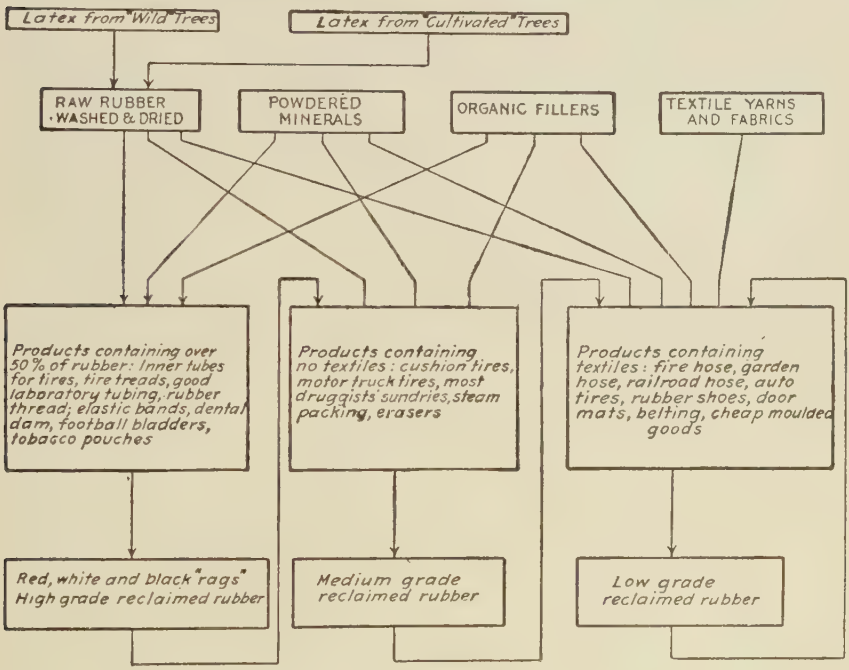
Latex from "Wild" Trees
Latex from "Cultivated" Trees
RAW RUBBER WASHED & DRIED
POWDERED MINERALS
ORGANIC FILLERS
TEXTILE YARNS AND FABRICS
Products containing over 50% of rubber: Inner tubes for tires, tire treads, good laboratory tubing, rubber thread; elastic bands, dental dam, football bladders, tobacco pouches
Products containing no textiles: cushion tires, motor truck tires, most druggists' sundries, steam packing, erasers
Products containing textiles: fire hose, garden hose, railroad hose, auto tires, rubber shoes, door mats, belting, cheap moulded goods
Red, white and black "rags" High grade reclaimed rubber
Medium grade reclaimed rubber
Low grade reclaimed rubber

FIG. 335.

it is returned directly to the original batch or compound without further treatment.

The automobile tire industry is to-day the most important branch of the rubber industry so far as the value of the product is concerned. Pearson estimates the consumption of rubber by the tire industry as over 71,000 tons in 1916. This is based on a statement of the Automobile Chamber of Commerce that there were in 1915, 2,400,000 cars in the United States and 714,000 cars outside of this country. It is estimated that the world total of scrapped tires in 1916 was 183,000 tons. The essential parts of an automobile tire are: the bead, frictioned duck, side wall, breaker strip, cushion, and tread. The compound used for each part is designed to render a special service and for this reason great care must be given to the writing of the recipes. The cushion compound must show high elas-

ticity; the tread compound must resist abrasion; the compound used for coating the duck (the friction compound) must possess a high cohesion value; the bead compound need possess none of the properties as it acts as a filler, givings rigidity to that part of the tire.

The official estimate of manufactured rubber goods in the United States shows that in 1916 these products were valued at over $300,000,000.

Some idea of the relation of size to weight of rubber belting can be formed when it is stated that a five-ply-rubber belt, 36 inches wide, 1411 feet in length weighed 9423 pounds. This belt is hung in the Government Terminal Grain Elevator, Vancouver, B. C.

Research Chemistry. Among the most important developments which connect theoretical chemistry with the practical manufacture of rubber-goods are: (1) The synthesis of rubber; (2) the introduction of organic vulcanization accelerators; (3) the treatment of low-grade rubbers in order to increase their strength and life, and (4) investigation of the chemistry of the vulcanizing process.

Synthetic Rubber. The first record of any attempt at preparing rubber in a laboratory is that of Bouchardat (France) who in 1879 claimed that he had polymerized isoprene to rubber by means of strong aqueous solutions of hydrochloric acid. Tilden (England) in 1882 claimed that he had produced rubber by treating isoprene with nitrosyl chloride. Kondakow (Russia) in 1901 published a paper on the polymerization of dimethyl-2, 3-butadien-1, 3 in which he described a product which was tasteless and odorless and which possesses many of the chemical and physical properties of rubber. In 1909, Fritz Hofmann and Carl Coutelle (Germany) stated for the first time the exact conditions under which rubber may be synthetized. The time and temperature required and the concentration of the solutions needed for its successful preparation. The patent describes a process for heating synthetic isoprene with or without the addition of neutral, acid, or alkaline catalysts at a temperature under 250° C. Harries (Germany) in 1905 defined the rubber hydrocarbon as a highly polymerized 1-5-dimethyl-cyclo-octadien-1-5 and in 1910 he published the first *scientific* paper on a Synthesis of Rubber from Isoprene. Perkins (England) in 1912 presented a paper on the "Production and Polymerization of Butadiene, Isoprene, and their Homologs." Working in conjunction with him Fernbach and Strange (France) proposed to prepare butyl alcohol and aceton at a low price from starch by fermentation. The successive stages of this synthesis are: Butyl alcohol—monochlor butane—dichlor butane—butadiene. Another method worked out by the Synthetic Products Company (England) may be outlined as follows: Aldehyde—Aldol–1.3.butyleneglycol—the dichloride of this glycol—butadiene—rubber. One of the most important observations thus far made was noted separately by Harries and by Matthews. This is the formation of rubber by treating isoprene or its analogs with a small quantity of sodium or metallic amalgam either in the cold or with

the application of moderate heat. In his papers of 1911 and 1912 Harries described substances which he designated "Normal isoprene caoutchouc," "Normal butadiene caoutchouc," "Normal dimethyl butadiene caoutchouc," "Sodium butadiene caoutchouc," "Sodium isoprene caoutchouc," and "Sodium dimethyl butadiene caoutchouc."

Synthetic rubber is "isoprene polymerized to a rubber-like substance." There are, however, certain other substances which must be classed as isomeric or homologous rubbers. The Elberfeld product was first tested out on a commercial scale in the Continental Kautschuk Fabrik in Hannover. Duisberg in 1912 at a meeting in New York City exhibited a hemisphere of this material weighing over 300 pounds.

Isoprene has been carefully studied by a number of chemists who describe it as a hydrocarbon having the formula C_5H_8, the boiling-point, 34° C., the specific gravity, 0.6989, at 0° C. On heating to 260° C. it polymerizes to dipentene. Although polymerization to rubber may occur at low temperatures, it appears that the products obtained at higher temperatures are more constant in composition.

Synthetic rubber research received its first great stimulus in 1910 when the price of "Up river Fine Para" rose to $2.90 per pound. To-day with high-grade smoked plantation rubber selling in New York City at about 60 cents per pound, the proposal to put an export tax on raw rubber in the British Colonies, and the uncertainty of shipments from the Middle East—the synthetic production of rubber within the United States has again received attention. There are at this time at least six large rubber-goods manufacturers who are conducting researches in this field.

Vulcanization Accelerators. After synthetic rubber had been prepared it was noted that it would not vulcanize in the usual manner and this was probably due to its extreme purity. The first published account of organic amino compounds used as accelerators of the vulcanizing process appears in a Patent granted to Bayer & Company in 1912. Piperidine was the substance first mentioned, but many other amino compounds have since been tried out with good results. The most commonly used material is amino-benzol (anilin) and its principal application is in the vulcanization of automobile tires. In this way the time of vulcanization has been cut down from seventy-five to fifteen minutes and the output of the factories has been proportionately increased. This is one of the discoveries which has made it possible for factories to turn out as many as 10,000 tires per day, using the same number of vulcanizing autoclaves as was formerly required for 3000 tires.

The substances thus far identified as "accelerators" include quaternary ammonium bases; para-diamino-benzol; piperidine; quinoline; urea derivatives. These substances, in general, constitute not more than 1 per cent of the total rubber compound.

Improvement of Raw Rubber. Spence and Russell propose to treat low-grade rubbers with metallic sodium while the rubber is free from

water (U. S. P. No. 1,112,938 issued 1914). In 1912 a method was proposed for improving "tacky" rubber by treating it with 5 per cent of a metal such as sodium, or a derivative such as sodium ethylate. The materials are mixed in a machine at a temperature below 100° C. and afterward washed with water.

The Vulcanizing Process. The principal observations which have thus far been made are: during the vulcanizing process a certain amount of the admixed sulphur is altered in such a way that it can no longer be extracted with aceton. This is designated "combined sulphur," while that which can be extracted is known as "free sulphur." No process is published at this time for the removal of the *combined sulphur* from a finished product. Vulcanization begins at temperatures as low as 50° C. and proceeds rapidly with increase of the heat. Rubber which has been vulcanized with sulphur chloride contains both sulphur and chlorine in chemical combination. Many chemists claim that vulcanization is a process of *adsorption*. Spence, Galletly, Scott and Young have conducted extensive experiments in order to obtain definite data on the chemical changes which take place and Hinrichsen has found that the concentration of sulphur chloride in cold vulcanization has little effect on the composition of the vulcanized product formed. Wo. Ostwald in 1910 brought out his "adsorption theory of vulcanization" and by means of it has explained many points. As there is an "adsorption equilibrium," all vulcanized rubber contains some free sulphur. He also shows that vulcanization is a "reversible process." As a matter of historical interest the name of Carl O. Weber should be mentioned as his investigations published in 1894 were among the earliest made in this field.

Gums Related to Rubber

Chicle. This is a gum obtained from the latex of *Achras sapota*, at present harvested chiefly in Mexico. The *Achras* known to the Maya Indians of Yucatan yields a milky sap which exudes when wounds are made in the rough bark. According to trade reports, the tree is found all over the peninsula. The trees yield on an average 6 to 8 pounds of gum. First-class, well-cooked chicle is nearly white when fresh and clean. If the gum is overcooked it turns reddish. Then again certain trees are known to yield a reddish gum under ordinary conditions. Good specimens are elastic, firm, aromatic and tenacious. Tschirsch was able to isolate at least six different substances from chicle, as follows: α-chiclalbane, m.p. = 220; β-chiclalban, m.p. = 158; γ-chiclalban, m.p. = 86; Chiclfluavil, m.p. = 66; chiclalbanan, m.p. = 56; and chiclgutta. Bosz and Cohen have also examined chicle, but they have chosen a different terminology for the substances isolated.

Chewing Gum. In 1910 there were imported into the United States *six million* pounds of chicle, nearly all of which was used in the manufacture of "chewing gum." For this purpose the cleaned and dried

gum is mixed with flavoring matters, pleasant smelling oils, and fillers. Darling has suggested the use of Pontianak gum for the manufacture of chewing gum, and this material is used for this purpose at present to some extent. Plantation crêpe rubber is also used after suitable treatment. The purification processes for chicle used in chewing gum must be such as not to affect the flavor or the plasticity or the weight of the gum to any marked extent. On the other hand it is most desirable to remove from the crude gum: silica, sand, bark and vegetable matter. The "color" of chewing gum has only an esthetic value.

The Analysis of crude chicle includes the determination of water, aceton soluble matter, gutta, and mineral matter. The determination of the viscosity of chicle solutions is now rocognized as an important criterion of the quality of raw chicle. This test is carried out in a Stormer viscosimeter. (See: Dannerth on "Industrial Chemistry of Chicle and Chewing Gum," J. I. E. C. 1917, July.)

Balata. This gum is obtained chiefly from *Mimusops globosa*, which grows in Dutch Guiana. It is the most important technical substitute for gutta-percha; in fact, no satisfactory methods for distinguishing one from the other are known at this time. Balata occurs in commerce as leathery elastic sheets which soften at 50° C., become plastic at 100° C., and melt at about 150° C. One commercial sample showed on analysis in round numbers:

Moisture	2.00 per cent
Ash	1.00 "
Resin, soluble in alcohol	42.00 "
"Gutta," soluble in chloroform	45.00 "
Residue	10.00 "

Boiling liquids remove varying percentages of soluble matter from commercial samples, as follows: Water, 5.7 per cent; alcohol, 41.5 per cent.; aceton, 42.5 per cent; ether, 87.00 per cent; chloroform, 87.00 per cent.

The material offered as gutta-percha is frequently the product of the *Mimusops* plant. Balata is at present used extensively in the manufacture of belting for power transmission. It appears to have an advantage over rubber belting, in that it is practically unchanged by exposure to high temperatures, such as would be encountered in ordinary power transmission. Balata is also used to a large extent in the manufacture of ladies' "dress-shields." Both gutta-percha and balata can be vulcanized after they are deresinated.

Pontianak. This gum is frequently designated "dead Borneo," or Jelutong, or Pontianak, after the port from which it is shipped. It is obtained from several species of *Dyera*. It occurs in commerce as a grayish-white mass resembling burnt lime. Closer inspection shows that it

contains large quantities of water. An analysis of the crude material as received at the factory showed (in round numbers):

Moisture	60.0 per cent
Resins	30.0 "
Rubber	10.0 "
	100.0 "

This material is washed, and dried in the air, and then mixed with oils or greases, in order to drive off the last portions of water.

Pontianak, because of its large resin content, is eminently well suited for the production of so-called "friction compounds" used for coating belting duck. It penetrates the interstices of the fabric very readily, and so makes possible a strong adhesion among the several layers of duck.

In 1910 a large company was financed in America for the extraction of the resins of pontianak on the island of Borneo, before shipment. The product of the factory is a sheet closely resembling the lower grades of wild rubber. The natural product is now exported in the original form (with resins and water). The market price of this crude product, in New York, January 1, 1914, was about $6.25 per 100 pounds.

Gutta-percha. This gum is obtained from the latex or milk juice of several trees found native in the Malay, Borneo, the Guianas and in New Guinea. The latex is coagulated by boiling it with acid juices in small pots. The principal gutta-yielding plant is *Palaquium gutta* (syn: *Isonandra gutta*, and *Dichopsis gutta*). The first note made of the properties of gutta-percha was by Montgomery in Singapore in 1832. Commercial samples soften at 60° C., liquefy at 140° C., and fuse just before vaporizing at 190° C. The gum is more or less soluble in ether, chloroform, carbon tetrachloride and carbon disulphide. It is insoluble in water. In the usual organic solvents the gum at first swells slightly to a transparent mass, and then yields, on shaking in the cold, a homogenous solution. Petroleum ether of boiling-point below 40° C. does not dissolve gutta, but it does dissolve the resins; hence this may be used for a determination of the latter ingredient in commercial samples. The specific gravity of gutta-percha and balata varies from 0.9604 to 0.9619. The resin content varies from 5 to 55 per cent and the softness increases with the resin content. Caspari found that sulphur chloride is absorbed by gutta and balata in the same way as by rubber. Sulphur was found by him to vulcanize all three hydrocarbons.

Gutta-percha is used by dentists for "temporary fillings"; the most important application is, however, in the insulation of submarine and subway cables. This was first proposed by Werner Siemens in 1847, and was the basis on which Cyrus Field in 1857 laid the first transatlantic cable. It is used for the "core" of golf balls, because of its lightness and

resiliency. Certain brands of ladies' "dress-shields" are lined with thin sheets of gutta, and in recent years similar "tissue" has been used by tailors as a cement for mending fabrics. For this purpose the thin sheet of gutta is placed between two layers of cloth and then partially melted by pressing with a hot sadiron.

LEGAL AND OFFICIAL CHEMISTRY

The vulcanization of rubber by means of sulphur was invented by Charles Goodyear of New Haven in 1839.

The vulcanization of rubber by means of sulphur chloride was invented by Alexander Parkes in 1846.

The reclaiming of rubber from vulcanized waste by means of acid was invented by J. K. Mitchell of Philadelphia in 1889 (U. S. P. No. 395,987.)

The reclaiming of rubber from vulcanized waste by means of alkali was invented by Arthur Marks of Akron in 1899 (U. S. P. 635,141). Suit was brought against the U. S. Rubber Reclaiming Works in 1915 and the patent was declared valid and infringed. (See Federal Reporter 225, 798; 227, 623; 229, 150.)

The solid rubber tire for horse-drawn vehicles was invented by Arthur Grant in 1896 (U. S. P. No. 554,675). After much litigation this patent was declared valid by the U. S. Supreme Court in 1911. (See I. R. W., May, 1916, 430.)

An improvement in vehicle tires was invented by E. C. Duryea in 1897 (U. S. P. No. 578,551). This patent was contested in a suit by the Buffalo Specialty Co. against the Indiana Rubber and Insulated Wire Co. in the U. S. Circuit Court of Appeals, VII District. (See Federal Reporter 334, 334.)

A method for vulcanizing rubber tires in a mold was invented by Peter Thropp in 1906 (U. S. P. No. 822,561). Suit for infringement was brought against the United States Tire Co. in 1915 and the patent was declared invalid by the U. S. District Court, S. D., New York. (See Federal Reporter 226, 941.)

The suit of a group of rubber-goods manufacturers against the National Board of Fire Underwriters related to the "labeling of Fire Hose." It was dismissed by the Supreme Court of New York in 1914. (I. R. W., March, 1914, 292.)

The suit of Rossbach against the Mansfield Tire and Rubber Co. related to a delivery of brown crêpe rubber. It was decided by the Supreme Court of New York, Ap. Div., for the defendant. (I. R. W., January, 1916, 171.)

The suit of the United States against the Michelin Tire Co. related to an importation of rubber goods. (Reports of the U. S. Court of Customs Appeals, April 24, 1911.)

The U. S. Court of Customs Appeals in 1911 held that reclaimed rubber is *not* a manufactured article.

"Rubber and Jelubong." U. S. Customs House decision. See Metallurgical and Chem. Eng. Journal, N. Y. March 15, 1918.

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CHAPTER XXXVI

VARNISH

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Definition. Varnish is a liquid, designed to form films to cover surfaces, which on exposure to the air hardens and forms a more or less transparent and glossy coating which improves or better displays the surface to which it is attached and to some degree protects it from dirt and injury.

Classes of Varnish. Varnishes may be divided into two classes: those which harden by evaporation of the solvent; such are spirit-varnishes; and those which absorb oxygen from the air and by chemical changes are made into hard films; these are oleo-resinous varnishes, and constitute the largest, most important and varied kind, used for a great variety of purposes.

Spirit Varnish. Spirit varnishes consist of suitable solids, dissolved in volatile solvents; the most important is shellac, which may be regarded as typical. It consists of shellac resin dissolved in alcohol, and when spread out in a film the alcohol evaporates, leaving the resin as a thin layer over the surface to which the varnish has been applied. It will be evident that the alcohol has served practically as a mechanical means of spreading the resin in a thin and uniform film; its cost is to be added to that of the labor, and the use and wear of utensils, required in applying the varnish, as all that we have at the end of the work is the film of resin.

Shellac Varnish. Gum-shellac, as the shellac resin is called, is usually in thin elastic flakes of a yellow or reddish or brownish-yellow color. Put a gallon of alcohol in a clean earthenware jar of two gallons capacity; at the close of the day's work gently drop into this three or three and a half pounds of flake shellac, without the slightest avoidable agitation; cover and let stand until the next day. Then with a clean wooden rod stir it for a few minutes, and during the day stir it for a minute at a time once an hour or so, and before night it will be dissolved. That is, the resin will be dissolved; but shellac naturally contains a little wax (4 per cent) which is insoluble and makes the solution milky

or muddy and opaque; the film is, however, transparent. Shellac may be bleached by dissolving it in an alkaline aqueous solvent and then treating it with chlorine; the shellac precipitates when the alkalinity is removed, and is white. This is dried and looks much like pieces of white candy; it cannot be dissolved in the manner described, as it is in lumps and sinks to the bottom; it is therefore dissolved by agitation, usually in a revolving barrel or churn; this is indeed the way orange shellac is made on a large scale. The latter is soluble in 85 per cent alcohol, though it is more satisfactory to use stronger; but white shellac already contains some water and requires 95 per cent alcohol.

Insoluble Shellac. White shellac is liable to pass into a modified form insoluble in alcohol; this especially is likely to occur if heated above ordinary temperatures or if kept in a dry place too long. For some purposes it is desirable to get rid of the five to ten per cent of water in white shellac before dissolving it; it is spread on trays in a drying room, but not heated very much; it is better to use artificially dried air at ordinary temperatures; in any case it must be dissolved as soon as possible.

Shellac varnish dries by the evaporation of the solvent, and appears to dry almost immediately; but some of the liquid is retained for a time, and it is not practicable to apply many coats in rapid succession, or it will be found that the whole has a waxy character, persistent and troublesome. Varnish made with "denaturized" alcohol is especially slow to dry; commercial wood alcohol is much better.

Damar Varnish. Alcohol is not the only solvent used in making spirit varnishes. Damar varnish is damar resin dissolved in spirit of turpentine, and dries by the evaporation of the latter. Both this and shellac are often adulterated with common rosin, or colophony. Damar may be dissolved cold, in a churn; some pulverize it before dissolving; or make it with the aid of heat, preferably in a steam-heated vessel. The varnish is a milky liquid, but may be cleared by filtration or otherwise. If made hot it can be cleared more easily. Five or six pounds of resin are dissolved in one gallon ($7\frac{1}{5}$ lbs.) of spirit of turpentine. The film is transparent and practically colorless.

Mastic and Sandarac Varnish. Sandarac is another resin usually dissolved in spirit of turpentine; another is mastic; both are also mostly soluble in alcohol. Amyl and methyl alcohols are for some resins better solvents than ethyl alcohol; and acetone added to alcohol greatly increases its solvent power.

Petroleum benzine is very commonly added to turpentine to cheapen it; it has the advantage of evaporating more readily and perfectly, and some of the heavier grades are for many purposes equal and perhaps superior to turpentine.

Pyroxylin Varnishes. Pyroxylin varnishes are a variety of spirit varnishes. The solid part is cellulose rendered soluble by acting on

it with nitric acid, making cellulose nitrates of various compositions. The principal solvent is amyl acetate, which may be extended or diluted with various liquids, as benzol, which have no real solvent action on the pyroxylin, but do not inhibit the solvent action of the amyl acetate; differing in this respect from the action of water on alcohol. Pyroxylin films are somewhat hard and stiff, and may be made more flexible by adding a fixed oil, as castor, cotton, or linseed, to the solution.

Lacquer. Spirit varnishes are often called lacquers, and are sometimes colored by aniline or other dyestuffs. Both asphaltum and coal-tar pitch are soluble in turpentine and benzine, or coal-tar naphtha, and are used as spirit varnishes; but more often with the addition of oil. Rosin is almost always added to asphaltum, but not necessarily.

Oleoresinous Varnishes. The greater part of the varnish made is compounded of oil, resin, and spirit of turpentine, and is of great variety of composition and uses. Almost all the oil used is linseed. A little tung, or Chinese wood-oil is used, but inconsiderable in amount as compared with linseed. This oil is usually subjected to some preliminary treatment; it is, as purchased from the makers, well settled and filtered, and free from cloudiness; it may be remarked that a mere trace of water causes a cloud, and the not uncommon belief that oil must be freed, by some treatment, from water and "mucilage" is a mistake, as oil of ordinary good quality is quite free from such things.

Breaking. Freshly-made oil, if heated to 400° F., suffers a slight partial decomposition; gelatinous clots appear in it, and it is said to "break"; this is due to the phosphates it contains, and any treatment which will destroy these will prevent its "breaking." A common way is to add, with agitation, a little sulphuric acid; the oil is afterward washed with water, and is found to be bleached somewhat; it may be bleached more by agitating warm, with fuller's earth, and filtering; but not all the color can be removed by any known means. What is known as "varnish oil" has been treated in some way so that it does not break; and if such oil is heated quickly to about 5 0° F. and cooled, it is found to be considerably bleached. This is a common practice. Sometimes a very little of some lead or manganese compounds are added before doing this. It is usually put through some such treatment and allowed to settle for a month or more before being used in varnish.

Weight of Oil. A gallon of linseed oil weighs 7.75 lbs.; but in selling oil by the barrel or larger quantities it is a commercial practice to call 7.5 lbs. a gallon, so that in buying it one gets about 3 per cent less in fact than the nominal amount. No charge, however, is made for the barrel —an oil-barrel is usually a 50-gal. cask—the value of which is usually more than the $1\frac{1}{2}$ gallons lacking. In making paint or varnish the full weight or measured gallon is always the unit.

Resins. Asphaltum is a mineral, but practically all the resins used in varnish are of vegetable origin, and most of them from tropical or

sub-tropical countries. They exude from trees, where the bark is injured, and form lumps varying in size from very small pieces up to masses of many pounds weight. In a few cases resin which is collected from living trees is used; but for the most part the varnish resins are dug up from the ground, the trees having fallen and decayed, and the lumps of resin having become buried, sometimes as much as six feet below the surface. Having for many years been thus buried they have undergone change, become harder and better suited for use. After being dug up, cleaned, and sorted, the resin is packed in boxes or bags, and in this condition market resins are bought at prices ranging from about 75 cents per pound for the choicest sorts to as little as 5 cents per pound for some inferior kinds. Probably a fair average price (1914) would be about 30 cents. The valuable qualities are clearness, hardness, high melting point, pale color, luster, and perfect solubility, after melting, in oil. As a rule these resins are not soluble in oil or in spirit of turpentine or benzine; but after melting they are found to be so changed that they dissolve in hot oil.

Melting Resins. Most of them require a temperature of 550 to 650° F. to melt them properly, and in melting they lose 10 to 25 per cent of their weight; some species lose more and some less; the best and hardest resins lose about 25 per cent. If this is done in the laboratory with proper precautions it will be found that the temperature of the melted mass is much higher than that of the vapor, showing that chemical decomposition has occurred. All light-colored resins darken on melting, some more than others. The greater part of the distillate can be condensed to a liquid; this is not done in this country, but in England and Europe it is common, partly because by refining the liquid may be made use of as a turpentine substitute, and partly because it prevents the escape of gases which may be thought objectionable in residence sections of cities.

Copal. Copal is a popular or trivial name applied to varnish resins, about as indefinite in its meaning as the term "metal." It was originally a Central American native word, and was applied to any resin. It is now used only for varnish resins, but does not designate any particular substance. In the varnish factory resins are commonly called "gums," although true gums, such as gum-arabic, are water-soluble. Colophony is always, and correctly, called rosin, and is never spoken of as a gum. Gum-varnishes mean oleo-resinous varnishes free from rosin.

Varnish Nomenclature. One hundred pounds of resin is the conventional unit, and varnishes are described as containing so many gallons of oil to this 100 lbs. of resin, weighed before melting. Thus a 20-gal. Kauri, or 20 K, is a varnish made from 100 lbs. Kauri resin, 20 gals. linseed oil, and (probably) 30 gals. spirit of turpentine, the amount of the latter not being mentioned. The grade of resin may also be mentioned; thus, "20 Brown 3 half benzine" would be 100 lbs. Kauri of the grade

known as No. 3 Brown Kauri, 20 gals. oil, 15 gals. spirit of turpentine (turps for short), and 15 gals. benzine. This is a fairly accurate description and any varnish-maker would recognize it. 100 lbs. of any resin counts for about 6 or $6\frac{1}{2}$ gals. in the batch; turps weighs 7.2 lbs. and benzine a little more than six lbs. per gal. So this would figure as follows:

100 lbs. resin	= 75 lbs.	= 6 gals.
20 gals. oil	= 154 lbs.	= 20 gals.
15 gals. turps	= 108 lbs.	= 15 gals.
15 gals. benzine	= 90 lbs.	= 15 gals.
	427 lbs.	= 56 gals.

Actually it will be more like 420 lbs. = 55 gals., because at least a gallon of the thinner will be lost by evaporation.

Varnishes are also classified as "long" and "short," the former having more oil than the latter. Naturally, this is a variable division; but, generally speaking, varnishes containing 20 gallons or more of oil may be spoken of as "long," and 12 gallons or less as "short." Long varnishes are elastic, short ones hard. The most important short varnishes are rubbing and furniture varnishes, and of the long are spar and wearing-body.

Spar varnish is so called because designed to varnish masts and spars of ships, and contains from 25 to 30 gallons of oil, and all hard resins, the best being half Kauri and half Zanzibar, or some approximate equivalents. Wearing-body is also called carriage-finishing and is the finishing or wearing coat for carriage bodies, and contains 30 to 35 gallons of oil; the wearing coat for the wheels and understructure being somewhat harder, 22 to 27 gallons and called "gear" varnish. "Marine" is usually a cheaper grade of spar, and as now made always contains some tung oil. "Hard-oil finish" is or should be a hard-drying and rather cheap rosin varnish for interior house-finishing, considerably inferior to the standard interior varnishes. "Coach" is cheap rosin varnish, never used in coach-painting; its name is illegitimately derived from coach varnish of former times, which was a rather quick-drying medium-grade varnish. "Gloss-oil" is a solution of rosin in benzine, about the poorest thing made in a varnish factory.

Floor varnishes contain usually 15 to 18 gallons of oil, and the oil and resin should be very thoroughly cooked together. Probably most of them contain tung oil; but the best of the floor varnishes made before its advent have not been excelled.

It is now not uncommon to hasten the drying of varnishes by placing the varnished objects in an oven or hot room, at a temperature of 40° to 55° C. (105° to 130° F.). Twenty-four hours is usually the time for baking, but in many cases the maximum temperature is maintained only six to eight hours, and allowed to fall gradually. Metal objects, as automobile bodies and railway coaches, are subjected to higher temperatures

than wooden ones. As the heat increases chemical action, these varnishes are often made without driers, and this makes them more durable; it also keeps the film in a semi-liquid state during oxidation, when it would otherwise be more like a jelly, and thus has the effect of making it more continuously adherent to the foundation, more impervious, harder and smoother; better in every way. The low fusion point of common rosin makes it a suitable ingredient in these varnishes, and good results are obtained with baking varnishes containing a considerable proportion of it; hence baking varnishes contain little or no drier and may have more rosin than would otherwise be admissible.

The most important changes in this industry which have occurred during the present century are due to the use of tung (or China-wood) oil. This not only dries rapidly, but makes film much harder than that of linseed oil, and has remarkable water-repellent quality. In its natural or raw state it is not used; if raised to a high temperature it becomes a jelly which is worthless; but if carefully heated for one or two hours at 205° to 217° C. (400° to 420° F.) it becomes more viscous, like stand-oil, and has acquired new qualities. To do this more safely it is customary to dissolve in it at least one-third as much rosin, by weight, as there is of tung oil; more commonly an equal weight or more. Thus a rosin varnish is made, which may be used by itself or added to a linseed oil and resin varnish. Some varnish-makers add linseed oil to the raw tung oil and cook the mixture, and then use it as they would linseed oil alone, to make oleo-resinous varnishes; but by far the more common practice is to make a tung-oil-and-rosin varnish.

These varnishes dry with remarkable quickness and will stand unusual tests; they are thought by some makers to be of great durability and probably they are when the exposure is so severe that no varnish will last long; but some of the most experienced makers insist that in ordinary usage they become hard and brittle with age, and cannot be depended on for very prolonged use.

Linoxyn. When linseed oil is exposed to the air, either by blowing air through it or by exposure in thin films, it is changed into an elastic substance, not sticky or greasy to the touch, called linoxyn. This is an oxidation product, and weighs considerably more than the original oil, probably about one-fifth more; different experimenters have reached various results. Its specific gravity is higher than that of the oil; and it is apparent that the latter has contracted in volume as well as increased in weight. This product is insoluble in oil and in turpentine and most of the other oil-solvents, and is the elastic ingredient of oil-paints and oleo-resinous varnishes. When oil is spread out in a film and exposed to the air it does not for some time appear to change, but after a certain time it rather suddenly changes into a semi-solid, gelatinous, sticky condition; up to this point, being a liquid, any contraction which may have occurred causes no notable change; but now a somewhat solid

film quickly forms, in which contraction produces a state of tension. It is obvious that if this film is at all inclined to be porous, contraction will open the pores, because it stretches the solid part of the film away from the openings; and this is probably the cause of the porosity of dry linoxyn films.

Porosity. If, therefore, we can add something to the oil which will act as a flux, and postpone this preliminary setting until the compound, by absorbing more oxygen, is in a more stable condition, we shall decrease the final porosity of the film. This is probably what we do when we dissolve a resin in the oil. The resulting compound—varnish—does not take its initial set until it is more completely oxidized, and the film thus formed is more nearly free from pores than a pure linoxyn film.

Varnish Films. Such a film has two other advantages. First, it is harder, and resists abrasion better, and it is smoother, which has the same effect; second, as the liquid varnish is more viscous than oil, it may be applied in a somewhat thicker layer, and a thick film is more lasting than a thinner one. The most obvious quality of a varnished

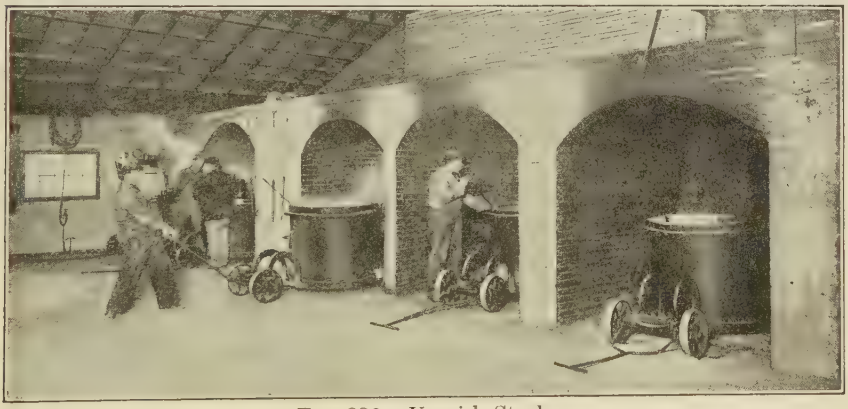

FIG. 336.—Varnish Stacks.

surface is its smoothness and lustrous appearance; its brilliancy depends not only on its smoothness but also on its high refractive power as regards light; those varnishes having the highest refractive indices being the most brilliant. This is increased, in general, by increasing the proportion of rosin.

Outfit for Making Varnish. The varnish-maker's outfit is very simple. A varnish-kettle is a cylindrical copper vessel, about 36 ins. in height and from 30 to 36 ins. in diameter, with a flat bottom. It has a loose cover, which is provided, in the middle, with an upright cylindrical outlet or "chimney" about 5 ins. in diameter and 8 ins. high; it has also a hole in it for a stirring-rod; and some styles have an opening for a large funnel. The kettle is loosely set on an iron truck or wagon, with three or four wheels, so built that the bottom of the kettle, which rests on a ring only slightly less in diameter than itself, is not more

an opening for a large funnel. The kettle is loosely set on an iron truck or wagon, with three or four wheels, so built that the bottom of the kettle, which rests on a ring only slightly less in diameter than itself, is not more than a couple of inches above the floor. There is a fireplace, consisting of a round pit sunk below the floor level, lined with fire-brick and having a grate, under which is an ash-pit and suitable air-flue, and nearly over which, a little in the rear, is a spacious chimney, Fig. 336, which carries off the products of combustion and also the vapor from the kettle. The fuel is coke, which burns freely and without much flame, which might set fire to the kettle vapor. The stirring-rod is of stiff steel, 5 or 6 ft. long, with a wooden handle. There is a large funnel, for use in pouring in oil, which may be put into the chimney in middle of the cover, or into a special opening in the cover near one side.

Varnish-Making. Into this kettle is put 100 or more commonly 125 lbs. of resin, the kettle is placed on the wagon, and wheeled over the hot fire. As the resin melts, the escaping gases cause foam, which makes it necessary that the kettle should be of considerable height and capacity. In about half an hour all the resin is melted; some varnish-makers melt with the thermometer in the melting resin, others depend on feeling the disappearance of lumps with the stirring-rod; and from time to time the latter may be withdrawn and the adhering resin examined. Without removing the cover, the oil, which has previously been heated in another receptacle, is added; some previously draw the kettle from the fire, others add the oil when the kettle is still on the fire. The oil and resin are cooked together, by the aid of the thermometer, until they are so combined that they will not separate on cooling; this is tried by putting a drop on a piece of glass or slate and if it clouds on cooling the combination is not complete. In fact it is common to cook varnish more than this; the more it is cooked the greater becomes its viscosity; and the more turpentine it will take to thin it to the proper consistency. Viscosity is spoken of by American varnish-makers as "body"; an American says a varnish has a heavy body when an Englishman says it is "stout."

Thinning. When sufficiently cooked, the oleo-resinous compound is, on the wagon, wheeled off to another room, well away from the fire, and a previously measured amount of spirit of turpentine (or benzine, or both) is slowly added with constant stirring. Varnishes are more or less colloidal solutions, and if some of these oleo-resinous compounds are thinned directly with benzine they form a swollen, gelatinous mass, insoluble in excess of solvent; while if a little turpentine is first added this makes a solution, which may safely be diluted with benzine if desired. Some makers add driers directly with the turpentine to the hot varnish, others wait until it is cool. These driers are compounds of lead and manganese. Fig. 337.

Proportion of Ingredients. Nothing has yet been said about the

quantity of oil to be added; in most varnishes it is the predominating ingredient. The larger the proportion of oil the more elastic and durable will be the varnish; the smaller the amount of oil, the harder, more lustrous, and quicker drying it will be.

Varnishes for furniture, which should be hard and brilliant, and free from the least tendency to tackiness, are made with 10 to 15 gallons of oil to the hundred pounds of resin; those for interior house varnishing contain from 15 to 20 gallons of oil; and for outside work, exposed to the weather, 25 to 30 gallons. These 30-gallon varnishes require about

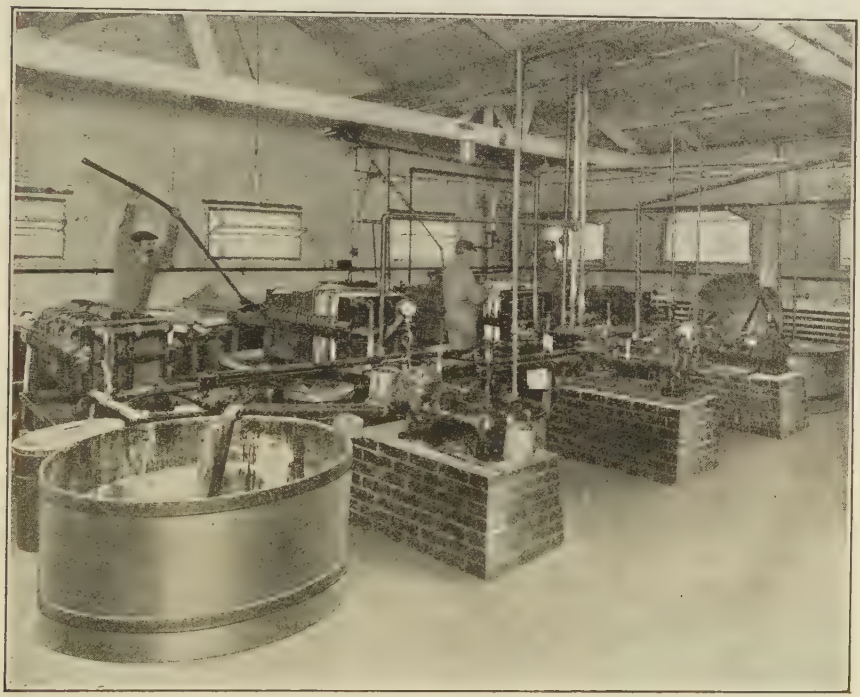

Fig. 337.—Varnish Filtration.

32 gals. of turpentine or other thinner; 10-gallon varnishes take about 25 gallons of thinner.

Rubbing Varnish. Rubbing varnishes contain 6 to 12 gallons of oil; they are so called because they become hard enough in from 1 to 6 days so that the surface may be rubbed with powdered pumice-stone, sprinkled on a pad of felt wet with water, until all the irregularities of surface are ground away, thus forming a smooth ("level") foundation for further coats of varnish. Those which contain even as much as 20 gallons of oil will in time become hard enough to rub; after which, by rubbing with finer materials, they may finally be polished; but this beautiful finish is not as durable as the natural gloss, which is always

left on work which is to be exposed to the weather. When one coat is applied over another it is always desirable to remove the gloss by lightly rubbing the undercoat, as the following coat does not stick well and smoothly to a glossy surface.

Rosin. Common rosin, or colophony, is extensively used in making cheap varnishes. It is not a natural resin, but is produced in the

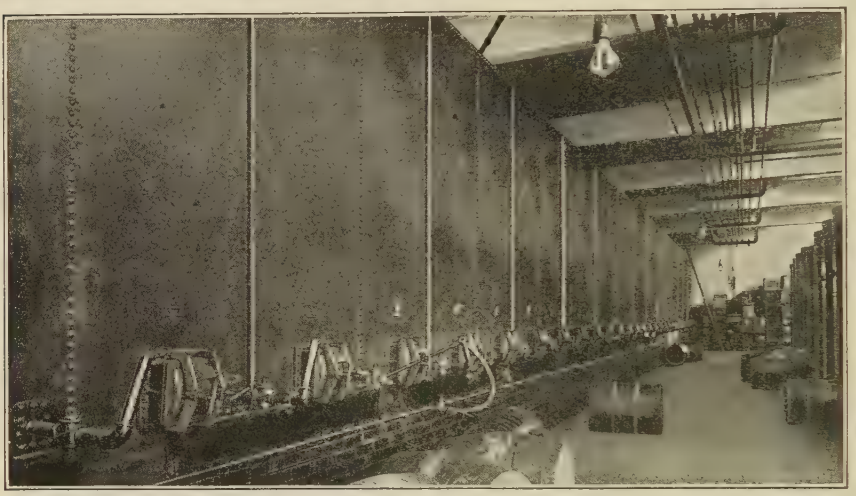

Fig. 338.—Varnish Storage.

distillation of crude turpentine, being the residue left in the retort after the spirit of turpentine is distilled off. It is an acid substance; and before use it is made nearly neutral by combining with it about 5 or 6 per cent of lime (calcium oxide). This makes it harder, more brittle, less easily fusible. It is made into oleo-resinous varnishes very much as are the natural resins, but with much more drier added; these varnishes are softer and less durable than the former class, but are mixed with them to make mixed varnishes of low price and medium quality. For some purposes rosin varnishes are used alone. They have good working qualities, and a small admixture of a rosin varnish to a "gum" varnish is often advantageous. They are made at lower temperatures than the "gum" varnishes; and the greater part of the tung or China wood-oil that is imported is used in rosin varnishes, on account of its superior drying qualities, in which it alone surpasses linseed oil.

Turpentine and Benzine. As to the comparative merits of turpentine and benzine (heavy petrolic ether), it may be said that without doubt turpentine is the better solvent. It is held more strongly by the oleo-resinous part of the varnish than is benzine, and hence evaporates more slowly, also it is naturally slower to evaporate. When varnish is applied with a brush it is impossible to avoid slight irregularities, slight ridges

and furrows, brushmarks, and if the volatile solvent evaporates very quickly these remain and show in the dried film; but with turpentine the coating remains liquid for a considerable time and these flow out and disappear before the varnish becomes viscid enough to retain its form. Other things influence this condition, but the nature of the volatile solvent is the most important factor. It should be said, however, that there are different qualities of benzine; and within a few years a comparatively heavy grade has been on the market, with a correspondingly higher boiling-point, less diffusive power, and more like turpentine in many respects; and to a great degree free from the objections which have always been urged against the lighter grades of benzine.

Pale and Dark Varnishes. To make a pale varnish it is necessary to have pale resins; but in some cases the paler pieces are softer and less valuable. The dark grades of the better kinds of resin, such as Kauri, are of excellent quality, and for many—in fact, most—purposes moderately dark varnishes are just as good as any. Even the dark varnishes (not black asphaltum) are transparent, and have an agreeable yellow or brownish red color; on dark wood they have even a better effect than paler varnishes, to which they are in every other respect equal. There are, of course, some dark resins of inferior sorts; and some of the best pale resins, such as Zanzibar, are of unequaled quality.

Baking-Japans. As the hardening of varnish is due to oxidation, it follows that with an increase of temperature the process will go on more rapidly. It is equally true that the solvent will evaporate more quickly from spirit varnishes in a hot atmosphere, so that it is generally true of all varnishes. If the temperature is high enough to melt the resin of a spirit varnish, or to keep an oleo-resinous compound in a liquid state until oxidation is nearly completed, the resulting film will be non-porous. Varnishes designed for such use are called baking-varnishes or baking japans; the best of them are the black japans in which the resin is partly asphaltum. These form coatings of great beauty and merit, strongly resisting both chemical and physical action. They are baked at varying temperatures; on wood, of course, at comparatively low heat, but on metal at as high as 400° F., though 300° F. is more common. The baking usually lasts three or four hours. The objects to be japanned are commonly dipped in the varnish and put directly in the oven. Since the drying is forced by the heat it is possible to use a varnish which would not dry at all (in any reasonable time) at ordinary temperatures, and such material is likely to be somewhat indifferent to chemical action.

Japan Driers. Another class of japans, having no relation at all to the preceding, are composed of linoleates or resinates of lead or manganese, usually containing free oil, and often some resinous or oleoresinous varnish,

and dissolved to a thin liquid with turpentine or more often benzine. These are also called driers; and they act by catalysis, inducing the rapid oxidation of the oil or varnish to which they are added. It is well known that lead and manganese form two classes of compounds; for example, a protoxide and a peroxide; and easily pass from one to the other. If they are present in the film in the higher state of oxidation they give up half their oxygen to the oil, then take up more from the air, and so act continuously as agents to pass along oxygen from the air to the oil. Manganese is more active than lead but each has its advantages. Driers may be made with other metals, such as nickel and cobalt, which readily pass from one state of oxidation to the other; but have no special advantages over lead and manganese. These compounds may be made by direct heating of the metallic oxides with oil or rosin, or by decomposing soaps with soluble salts of these metals. If by use of these compounds we introduce into oil even as small an amount as $\frac{1}{100}$ of its weight of these metals, the effect is very marked. The use of too much drier is objectionable, since it is likely to continue to act, slowly of course, after the film has hardened, and in time destroy its elasticity and coherence. Driers are not used in spirit varnishes, nor usually in baking japans.

Boiling Oil. Long-continued heating causes linseed oil to dry with a gloss, and oil which has been heated with a little lead and manganese oxides is called boiled oil; the untreated oil is called raw oil. Films of raw oil take 5 or 6 days to dry hard enough to be handled; while boiled oil will dry in 24 hours. For special purposes, however, oil is boiled for a longer time, and in this way is made the varnish used on patent leather and for some other uses.

Lithographic or " Stand " Oil. Linseed oil which has been bleached or otherwise refined so that it does not " break," is heated to a high temperature, usually 600° F., or higher, for a considerable time; it is then found to be viscid, like molasses; as it is heated without the addition of driers it is not what is called " boiled oil "; it is treated best in enameled kettles or aluminum- or silver-plated copper kettles, so that it is not much discolored. This is in this country generally called *lithographic oil*, in Europe *stand oil*. It dries with a gloss; and is sometimes used for making enamel paints, being regarded as equal to a varnish. It is largely used in Europe in varnish-making, the melted resin being dissolved in it; such a varnish requires less cooking than the more ordinary ones, and rather more turpentine or other thinner. They are pale in color; but American varnish-makers think they are less durable, the oil being too much changed, and not sufficiently combined with the resin. Stand oil is largely used in Europe in paint-making also.

Driers are sometimes added to varnish after it is made. The varnish is warmed to 100° F. to 150° F. and agitated for several hours with powdered litharge and some powdered manganese compound, either borate

or oxide. These lead and manganese compounds are dried immediately before use by heating them until it is certain that all the water is driven off. The amount used is considerable, 2 or 3 per cent, as that which is not absorbed will settle or can be filtered out.

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Varnish Vehicle. Ellis. C.A., **6**, 638. Sample dissolved in benzine, twice warmed, metallic salts dissolved with 5 per cent HCl, then det. by Fahrion's method. When copal is present, saponify, extract with ether.

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CHAPTER XXXVII

SUGAR

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Introductory. Highly refined commercial sugar consists of sucrose. The word "sugar," as used in this article and commercially, refers to sucrose of various degrees of purity.

Sucrose is widely distributed in the vegetable kingdom; two plants, however, supply practically all of the world's sugar. These are the sugar-cane (*Saccharum officinarum*) and the sugar beet (*Beta vulgaris*). Cane is grown throughout the Tropics and in some sub-tropical regions; the beet is produced in most parts of Europe, the northern and Pacific coast States of this country and in Canada. Very little sugar is produced in the British Islands, though excellent beets have been grown there experimentally.

Other plants producing commercial quantities of sugar are certain palms and the maple tree. For the purposes of this article it is only necessary to consider the two preponderating branches of the sugar industry, the cane and the beet. These two plants now produce nearly equal proportions of the world's sugar supply.

In sugar manufacture all substances contained by the plant juices other than sucrose are considered to be impurities. The word "impurity" is used in this sense in this chapter.

Cane Sugar

Raw Material and its Preparation. The raw material, sugar cane, is botanically a large grass. The approximate composition of the stalks, the part of the plant used in sugar manufacture, is shown in the following table by Dr. Charles A. Browne, Jr.,[1] and represents Louisiana cane during the manufacturing season. Tropical cane probably varies but little from this analysis except as regards the sugars, fiber and water content:

[1] "Hand-book for Cane Sugar Manufacturers," Spencer, 6th Ed., p. 5.

Water	74.50		74.50
Ash	0.50	Silica, SiO_2	0.25
		Potash, K_2O	0.12
		Soda, Na_2O	0.01
		Lime, CaO	0.02
		Magnesia, MgO	0.01
		Iron, Fe_2O_3	trace
		Phosphoric acid, P_2O_5	0.07
		Sulphuric acid, SO_2	0.02
		Chlorine, Cl	trace
Fiber	10.00	Cellulose	5.50
		Pentosans { Xylan	2.00
		Cane gum ; Araban	0.50
		Lignin bodies, etc	2.00
Sugars [1]	14.00	Sucrose	12.50
		Dextrose	0.90
		Levulose	0.60
Nitrogenous bodies (Total N = .06 per cent)	0.40	Albuminoids	0.12
		Amids (as asparagin)	0.07
		Amido acids (as aspartic)	0.20
		Nitric acid	0.01
		Ammonia	trace
		Xanthin bodies	trace
Fat and wax	0.20		0.20
Pectin (gums)	0.20		0.20
Free acids	0.08	(malic, succinic, etc.)	0.08
Combined acids	0.12	(malic, succinic, etc.)	0.12
Total	100.00		100.00

The cane grown in tropical countries usually contains an average of approximately 14.5 per cent sucrose, little or no levulose (when mature) and in all less than 1 per cent of reducing sugars. The fiber ranges from 10 to 12 per cent and even higher.

The cane is propagated from pieces of the stalk, termed "seed," which are planted in furrows or in clumps according to soil conditions. The young plants sprout from the buds at the nodes or joints of the cuttings and quickly establish themselves, soon forming large clumps and thick, almost impenetrable rows. The plant matures in the dry season in the Tropics and is harvested at this time. It never reaches full maturity in sub-tropical countries and is harvested for the manufacture of sugar in the autumn.

[1] The presence of raffinose has been reported but not confirmed (G. L. S.). The reducing sugars are grouped under the term "glucose" in cane sugar factories.

The stalks are cut close to the ground, freed of their leaves and the top joints are removed at the highest one showing signs of maturity. This point is determined by the color of the stalk. The clean stalks are removed to the factory as soon as possible after cutting. In Louisiana, however, owing to danger of frost damage late in the season, the stalks are cut and covered or windrowed and left in the fields until needed. This is not feasible in the tropics, as the cut cane would soon ferment if left in the fields, and must therefore be promptly milled.

The stubble is left to produce a crop of ratoons, to be harvested the following season, and where soil and climatic conditions are favorable, several successive crops may be secured from one planting. But one ratoon crop is usually harvested in Louisiana.

Until recent years the true seed of the cane was not known to be fertile, but since the discovery that cane does produce some fertile seed, extensive experiments in the culture of seedlings have resulted in a number of new and valuable varieties of canes.

In the preparation of the stalks for milling it is very desirable that they be freshly cut and that all leaves (trash) and immature joints be removed, since the trash reabsorbs juice in the milling process, and the unripe joints contain little sucrose and much invert sugar. Unfortunately labor conditions are usually such that the cane does not reach the mills in a clean state and freshly cut.

Manufacturing Processes. These processes include the extraction of the juice from the cane, its purification, concentration, crystallization of the sugar, and the separation of the crystals from the mother liquor (molasses).

Extraction of the Juice. The milling process is used almost without exception for the extraction of the juice. The diffusion process, described farther on in connection with the beet sugar industry, is no longer used, except in perhaps a half dozen factories.

As the cane arrives from the fields, it is unloaded upon an elevator consisting of endless chains with projecting arms or upon a belt-like conveyor composed of endless chains and wooden slats. In several unloading devices, the loaded cane car is tilted endwise or sidewise by hydraulic power and the load is discharged upon the elevator or conveyor.

The conveyor delivers the cane into a preparatory machine called a shredder or crusher, according to its type, which tears it into shreds or crushes it. The Fiske or National shredder, the pioneer of these machines, has two corrugated steel rolls driven rapidly in opposite directions, one at a higher speed than the other. The rolls nearly touch one another and strong springs at the bearings permit them to separate with a heavy feed of cane. This machine tears the cane into fine shreds; the juice extracted is immediately reabsorbed. Crushers also have two corrugated steel rolls driven in opposite directions but at the same speed. The corrugations are small and have sharp edges. The crusher rolls revolve very

slowly, crushing the cane and expressing about one half the juice it contains. The Krajewski and Fulton are well-known types of these machines. A Fulton crusher is shown in Fig. 322 in combination with a twelve-roller mill.

The rind and joints of the cane are very hard and offer great resistance in milling, hence the desirability of first breaking up the cane by machines requiring comparatively little power.

Cane mills are composed of various combinations of very heavy cast-iron rollers arranged in suitable massive cast-iron or cast-steel housings.

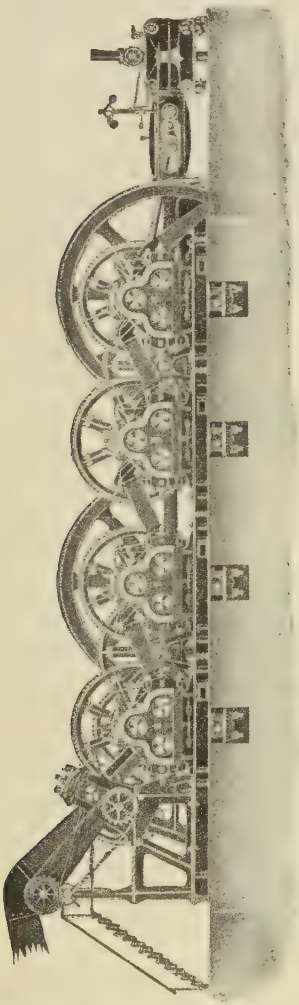

Fig. 339.

In modern installations the mills each have three rollers, and combinations of three-roller mills make up those of six, nine and twelve or more rolls. The entire system is driven with one or more engines. The crusher and mills shown in Fig. 339 are geared for driving with a single engine. The use of a single engine is not usual in the large installations of cane-mills in Cuba. Hydraulic rams are usually used to regulate the pressure on the rolls. The rams are shown under the crusher and mills in the illustration.

The following dimensions are typical of the large mills now in use: Rollers 36×84 ins. long; roller shafts, hollow nickel-steel forgings; journals 17 ins. diameter×21 ins. long. These dimensions are often exceeded, though few mills are now made with rolls longer than 84 ins. The weight of such a top roller with its shaft is approximately 14 short tons.

When the hydraulic pressure is applied to the top roll, as is usual in the majority of installations, the following loads upon it are about the customary numbers: 1st mill, 500 tons; 2d mill, 400 tons; 3d mill, 425 tons. These loads are often exceeded with very strong mills. Recent Hawaiian practice differs from these numbers approximately as follows: 1st mill, 500 tons, 2d and subsequent mills, 230 tons. It is the object to crush the cane as thoroughly as possible at the beginning, so as to better prepare the bagasse to receive the saturation water. These loads apply to rolls 84 ins. in length.

The mill rollers are so arranged that the cane is crushed twice by each 3-roll mill, and at each successive crushing the cane passes through a smaller

opening than before. The last mill is usually "set" with its back or bagasse roll and the top roll almost touching one another, or to use the factory term, "iron to iron." A curved knife or turn plate guides the crushed cane from one pair of rolls to the next. Notwithstanding the great strength of mill rolls and shafts these are often broken by the straining to which they are exposed.

More than one engine is used in operating the mills in present Cuban practice. This multiple use of engines facilitates the grinding of large quantities of cane with high efficiency.

The rinds and joints of the cane are very hard and offer great resistance in milling. Further, good penetration of the saturation water requires that as many as possible of the juice cells be broken in the first stages of the grinding. The crushers that have been described are designed to effect this destruction of the cells. An advance has recently been made in both Cuba and Hawaii in the preparatory crushing and shredding.

The Fulton crusher is now also made double, i.e., the cane passes through one crusher and directly into a second. The double crushing greatly increases the capacity of the milling plant and materially improves the extraction of the sugar. The first crusher is driven by a separate engine and the other by the engine that drives the first two or three mills.

The Hawaiian improvement is in the addition of a Searby shredder. This machine is a modification of a hammer mill in which a large number of hammers beat upon the cane and separate the fibers. This shredder may operate directly upon the entire cane or upon that broken by a crusher. Compared with Cuban practice, a small hourly cane-grinding capacity is required of the mills in Hawaii. The small grinding rate facilitates obtaining a high extraction, this number often passing 98 per cent with the combination of Searby shredder and multiple mills.

A recent Cuban plant consisting of two crushers and 15 mill rolls, all Fulton, has shown a capacity exceeding 125 tons of cane per hour, with an extraction of 94 per cent of the sugar in the cane. The mill rolls are 7 ft. long by 36 ins. diameter. The first crusher is operated separately, the second in combination with three mills and the last two mills are driven by one engine. Limitations of the boiling house have prevented ascertaining the full capacity of the plant as regards cane and extraction.

Where large capacity is necessary, it is considered advisable to use a long train of mills and drive the crusher by one engine, the intermediate mills by a second and the last two mills by a third engine. This arrangement increases the flexibility of the train and facilitates the speed adjustment of the various rolls so that they operate in harmony.

A further marked improvement in milling, since the earlier editions of this book, is in the grooving of the mill rolls. Formerly small circumferential grooves, spaced about six per inch, V-shaped, were turned in the roll shells. The size of the grooves has been gradually increased and now frequently but three per inch are used. A decided gain as regards cane

capacity and juice extraction has been secured by turning very deep narrow juice grooves in the shell of the feed or cane roll at intervals of about 2.5 inches. These grooves are about 1.5 ins. deep. The bagasse bridges over the grooves and the juice is forced into them. Similar grooves, but much smaller are cut in the discharge or bagasse rolls. This type of groove is known as the " Messchaert," after its patentee. A similar result is obtained with the Hind-Renton grooving. These grooves are V-shaped, the included angle being 30°. The grooves are spaced two per inch and facilitate the passage of the cane and the removal of the juice.

It is altogether probable that the introduction of double crushing and the deep juice grooves will lead to the use of much longer mill rolls and consequently to larger cane capacity. Modern materials and methods of construction overcome the objections that formerly held against the use of long rolls. Further, moderate roll pressures are necessary where thorough crushing or shredding is practiced and the shafts can therefore be made of ample strength.

Water is usually applied to the crushed cane or bagasse, as it is now termed, as it emerges from the rolls of the first and second mills. The bagasse is in the condition of a sponge that has been squeezed nearly dry and quickly absorbs the water, which dilutes a part of the remaining juice. The subsequent milling of this moistened bagasse extracts more sugar than would be obtained with dry crushing. The water is often all applied to the bagasse from the next to the last mill and the thin juice from the last mill is pumped back upon the bagasse from the first. There are various modifications of this method, depending upon the number of mills in the series. In this method, all the juice extracted by all except the last mill is pumped to the defecating apparatus for the next stage of the manufacture. This use of water on the bagasse is termed " saturation," " maceration " or " imbibition."

The final residue is known as " bagasse " or, in the English colonies, " megasse." It is conveyed directly from the mills to special furnaces, where it is burned for the generation of steam in the boilers. All modern cane factories are operated by steam.

The bagasse, with very good milling, contains about 50 per cent marc or woody fiber and less than 46 per cent moisture. Good bagasse has a fuel value of from 2700 to 3000 B.T.U.'s, and in many tropical plants supplies all the fuel required in the manufacture. The majority of factories must supplement this fuel with wood, coal, or oil. The cane factory requires a boiler installation of approximately150 H.P. per 100 tons cane ground per twenty-four hours. This number depends upon the efficiency of the plant, the quality of the cane and the class of sugar manufactured.

The loss of sugar in the bagasse varies greatly in different establishments, but with an installation consisting of a crusher and four 3-roller mills, and the use of saturation water, it approximates 4 per cent sucrose in the residue or in terms of the original cane, 1 per cent. With

excellent milling and liberal saturation (25 to 30 per cent water) more than 96 per cent of the sucrose in the cane may be extracted in the juice. These numbers all indicate much better results than are obtained with the average equipment. Where local conditions of cost of cane and value of product justify additional manufacturing expense, the extraction may reach 98 per cent and the bagasse contain less than 2 per cent of sucrose.

The yield of juice by milling varies with the quality of the cane itself. Woody canes yield less juice than those of low fiber content and immature canes more than ripe, rich stalks. By dry crushing, i.e., without saturation, 75 per cent of the weight of the cane in juice may be readily obtained with the immature canes of Louisiana, whereas in the tropics it usually requires very heavy milling and liberal use of saturation water to express an equivalent quantity.

The present tendency is toward the construction of very heavy milling plants with rolls 78 to 84 ins. long and arranged with a crusher and three to five strong mills set "tandem." Great attention is paid to the foundry mixture in casting the rollers, to obtain an iron that is neither too hard nor too soft, and that will retain a slightly roughened surface that reduces the tendency of the cane to slip and clog the mill. Such mills will grind from 1500 to 2000 tons or more of cane per twenty-four hours, though where a very large extraction is desired the smaller number is that usually reached.

Purification of the Juice. The juice as it flows from the mills is turbid and filled with impurities, both chemical and mechanical. It is first strained through perforated brass sheets having 400 round holes and upward per square inch. The surface of the strainer is cleaned by mechanical scrapers, which deposit the fiber and trash upon one of the bagasse conveyors, to be again passed through a mill.

Defecation Process. The next stage of the purification is the defecation process. The raw juice is always of acid reaction. This acidity is neutralized with milk of lime, dry slaked lime, or powdered quick-lime and the juice is then heated to coagulate the albuminoids.

In the ordinary method of defecation, the juice is first limed in mixing tanks, to slight alkalinity or faint acidity, according to the grade of sugar to be made, and is then conducted to defecators. These are tanks fitted with steam coils or steam jacket at the bottom. Many factories lime the juice in the defecator. The limed juice is now heated with steam. The heat is continued until a heavy blanket of scum rises to the surface and breaks or "cracks." When the cracking point is reached the heat is discontinued and the juice is left at rest for the precipitates to settle. This process separates nearly all of the albuminoids, partly by coagulation, and a part of the acids, fat, wax and gums. Some lime salts are formed and persist throughout the manufacture. A part of these salts subsequently deposit upon the heating surfaces of the evaporating apparatus. If the process is conducted with care, there is no decomposition of the sugars,

but with excessive liming the invert sugar is decomposed in part and forms dark, bitter compounds with the lime. These lime salts impede the crystallization of the sugar. The ripe cane frequently contains no levulose, but this sugar always appears in the molasses, even if no sucrose is inverted, and is attributed to the action of the salts upon the dextrose. In an acid defecation, as in making white sugar, if insufficient lime is used, inversion of sucrose occurs.

After allowing sufficient time, usually an hour or longer, for the subsidence of the precipitates, the clear juice is decanted from between the blanket of scum and the mud at the bottom of the defecator. The clear juice is run into storage tanks preparatory to the evaporation. The scum and mud, mixed together, are pumped into filter presses and the filtrate is added to the clear juice already obtained. The press-cake is used as a fertilizer or on many estates is wasted. The sugar content of the cake is reduced by either washing it with water while still in the press or by removing the cake, beating it to a cream with water and refiltering. The unwashed cake contains from 8 to 12 per cent of sugar, according to the richness of the cane and the quantity of water used in washing the mud from the defecators, and that by refiltration or thorough washing contains about 1 per cent.

The filter press is that used in other industries. A frame press of a type very generally used in sugar factories is illustrated in Fig. 16. A heavy jute or cotton cloth is placed over the grooved or perforated plate shown next to a frame, in the figure. When all the plates are covered in this way and the press is closed a series of cloth-separated chambers is formed. The muddy juice is forced into these chambers under a pressure of 40 to 50 lbs. The cloth retains the precipitates and the filtrate flows from cocks connected with channels in the grooved plates.

In the manufacture of plantation white sugar, in Louisiana and to a limited extent elsewhere, the raw juice is saturated with sulphurous acid, then limed to faint acidity to litmus. The rest of the defecation process is conducted as already described. In making the refining grades of sugar, sulphur may or may not be used, and is not generally employed in tropical factories. An acid defecation is usually made in Louisiana and an alkaline one in the Tropics, where lime is usually added so long as a precipitate forms. The process is termed " clarification " in Louisiana.

Phosphoric acid or acid phosphate of lime is often used in the defecation, especially in making white and high-grade yellow sugars, to form a voluminous precipitate, which carries down much flocculent and some coloring matter.

The defecation may also be conducted by a continuous process, in which there is a constant flow of limed and heated juice through a special form of settling tank. These tanks are so arranged that the mud is drawn off at the bottom and the clear juice at the top. An objection to this method is the danger of decomposition or inversion of sugar. Certain spores

persist notwithstanding the high temperatures and, since mud or juice may lag in the settler, loss of sugar may occur. The present tendency in the manufacture is to use the ordinary or intermittent defecation process. This involves frequent cleaning of the tanks.

Sulphitation Processes for White Sugar. Plantation white sugar is made in Louisiana by the acid defecation process described above. The defects of this process are that it involves some loss of sucrose by inversion and difficulty in producing a sugar of uniformly good color.

A modification of the sulphitation process that involves no inversion of sucrose and produces a fairly uniform product is conducted as follows: From 13 to 15 gallons of milk of lime of 26.6° Brix is added to the cold juice. This is now saturated with sulphurous acid gas obtained by burning sulphur in a special stove. The sulphitation is stopped when the juice is neutral to phenol-phthalein and heat is then applied to it until its boiling-point is reached. A voluminous precipitate is formed which is separated by settling and decantation or by filter-pressing.

The clean juice is evaporated to a syrup of 54° Brix. The syrup is cooled to air temperature and then sulphited to faint acidity, after which it is heated to about 90° C. to break up lime salts. The hot syrup is run into settling tanks preparatory to the vacuum pan work.

In the Bach sulphitation process the preliminary work is similar to the above except that a little less than half the quantity of lime is added to the juice. The precipitate is removed by settling and decanting. The clean juice is evaporated to a syrup of 54° Brix. The syrup is cooled to air temperature, sulphitation is started and then milk of lime of 26.6° Brix is added to it in the proportion of 16–17 gallons per 1000 gallons of syrup. The sulphitation is continued until the syrup is neutral to phenol.

The sulphited syrup is filter-pressed and the cake is washed to low sucrose content while still in the press. No difficulty is experienced in the filtration. The filtered syrup is heated to about 94° C., and is then cooled and sulphited to slight acidity. An acid reaction is necessary in order to form the acid sulphite of lime and thus prevent the precipitation of lime during the crystallization of the sugar. The syrup is now ready for the vacuum pan.

The Carbonation Process. The carbonation process, described farther on in the beet-sugar section, modified as to quantity of lime and temperature conditions, is used to a very limited extent, except in Java. In treating cane juice by carbonation very little lime is used as compared with beet-sugar work, and the temperature is kept below 55° C. to prevent the decomposition of the invert sugar which occurs in the presence of lime at higher temperatures. Single carbonation may be used in treating cane juice, but never that of the beet.

In the application of carbonation to the manufacture of plantation white sugar it is modified only by the addition of sulphitation.

Either the single or double carbonation may be used, though, theoret-

ically at least, the double process is preferable. The procedure is as follows: The matter of costs decides which carbonation method shall be used. The single process requires less carbonic acid, lime, filter cloth and labor. It possibly produces less sugar than the double process, but the reduction of costs probably usually offsets the reduced yield. The single carbonation is conducted in the cold precisely as a second carbonation or saturation, except as to the addition of lime. Approximately 0.75 per cent of lime (CaO) figured on the weight of the cane, is slaked and reduced to a milk of 35.7° Brix, and is added to the raw juice and this is then carbonated to neutrality to phenol.

In the double carbonation, approximately 2.5 per cent of lime is added to the raw juice and is then carbonated until there is a sharp separation of the precipitates. The juice is now filter-pressed. The filtrate should retain an alkalinity figured as lime (CaO) of 1 to 1.5 grams per liter. The filtered juice flows to the second carbonation or saturation where it is again carbonated in the cold, this time to neutrality to phenol. Near the close of the saturation, the temperature is gradually increased and when the neutral point is reached, it is quickly raised to about 75° C. The juice is now filter-pressed.

As may be noted, the first carbonation is stopped in the double process before there is danger of decomposing the precipitates, whereas in the single process there is always this risk. If magnesia be present in the lime, it is removed in the double process, since its carbonate is insoluble in a strongly alkaline solution.

After filtration, the juice is cooled to the air temperature and both it and the syrup are sulphited as in the sulphitation processes.

Evaporation. The purified juice is next evaporated to a syrup of about 54° Brix (30° Baumé). The evaporation is conducted in multiple-effect vacuum evaporators.

There are several types of multiple-effect evaporators, but the basic principle of all is the same, so only the so-called and commonly used standard type of apparatus with vertical tubes will be described. The triple effect is the combination generally employed. The evaporating vessels or " effects " of this combination, three in number, are vertical cylinders somewhat of the form of the vacuum pan shown in Fig. 340. In the lower part is a belt containing vertical brass or copper tubes through which the juice circulates, and which are surrounded with steam. This heating belt is termed the " calandria." The vessels of the triple effect are arranged so that a vacuum may be maintained in each, e.g., 5 ins. in the first effect, 14–16 ins. in the second, and 26 ins. or as high a vacuum as can be secured, in the third. Exhaust steam from the various engines of the factory is used to heat the juice in the first effect; the steam generated in boiling this juice is conveyed through the vapor pipe in the dome of this vessel to the heating calandria of the second effect. Juice is conducted from the first vessel to the second and from the second to the third. The vapor from the

first effect boils the juice in the second by reason of the differences in vacuum and boiling-points, and the condensation of this vapor produces the vacuum in the first vessel. In the same way the liquor is boiled in the third vessel and the condensation produces the vacuum in the second. The vacuum in the third effect is produced by a pump and condenser. The water of condensation is removed by pumps, except from the first calandria, from which it flows by gravity. The evaporation is so conducted that a stream of juice is fed into the first vessel and flows from effect to effect, gaining in density as it travels, and finally finished syrup of the desired density is constantly pumped from the third effect. This method is often extended to four vessels, which is termed a "quadruple-effect," and so on. For various reasons, the vertical tube or standard type of evaporator is not often extended beyond four vessels in cane factories. The water from the steam condensed in the calandrias is used for boiler feed-water and the surplus for maceration of bagasse and other purposes, thus utilizing its heat.

The method of producing the vacuum will be described later in connection with the crystallization of the sugar.

The differences of vacuum and the consequent differences in boiling-points of the liquors enable the multiple-effect use of the steam applied in the calandria of the first vessel. A triple-effect apparatus will evaporate about 3 lbs. of water per pound of steam applied in the calendria of the first vessel; a quadruple-effect will evaporate about 4 lbs. and so on. The first vessel is frequently built with much larger heating surface than the others, that it may generate extra vapor for use in juice heating or vacuum pan boiling. The extra steam generated in the first vessel is circulated through the juice heater and raises the temperature of the juice to about the boiling-point. A part of the juice is evaporated in double-effect and all the juice is heated with similar economy. A separate vessel, termed a pre-evaporator or preheater, is often employed to increase the evaporative capacity and economize fuel, by heating juice in double-effect, and in boiling a calendria vacuum pan, thus extending multiple-effect evaporation to the massecuite. The preheater itself may be in double-effect or extra vapor may be taken from the second vessel of the evaporator. This gives triple-effect juice heating or vacuum pan boiling.

Crystallization of the Sugar. The concentrated juice or syrup is pumped from the multiple-effect to storage tanks preparatory to the crystallization of the sugar. The crystallization is accomplished in a single-effect vacuum pan such as is shown in Fig. 340.

The vacuum or strike pan, Fig. 340, is a cylindrical vessel, *A*, usually of cast iron, having a dome-shaped top with vapor pipe, *B*, and a conical bottom provided with a strike or discharge valve, *C*. The pan is equipped with large heating surface of copper, and steam and vacuum gauges, also sight-glasses, *D*, for watching the progress of the work, a proof-stick for drawing test samples and suitable pipe connections for syrup and

molasses. The steam enters a manifold, *E*, from which it is distributed to the coils; each of the latter has a stop valve for steam, and drainage connections for condensation water. The vapors from the boiling sugar solution pass through a save-all, *F*, connected at the bottom with the pan, where they expand and meet baffle plates, so that sugar entrained with the vapor may be returned to the apparatus. The vapors from the evaporat-

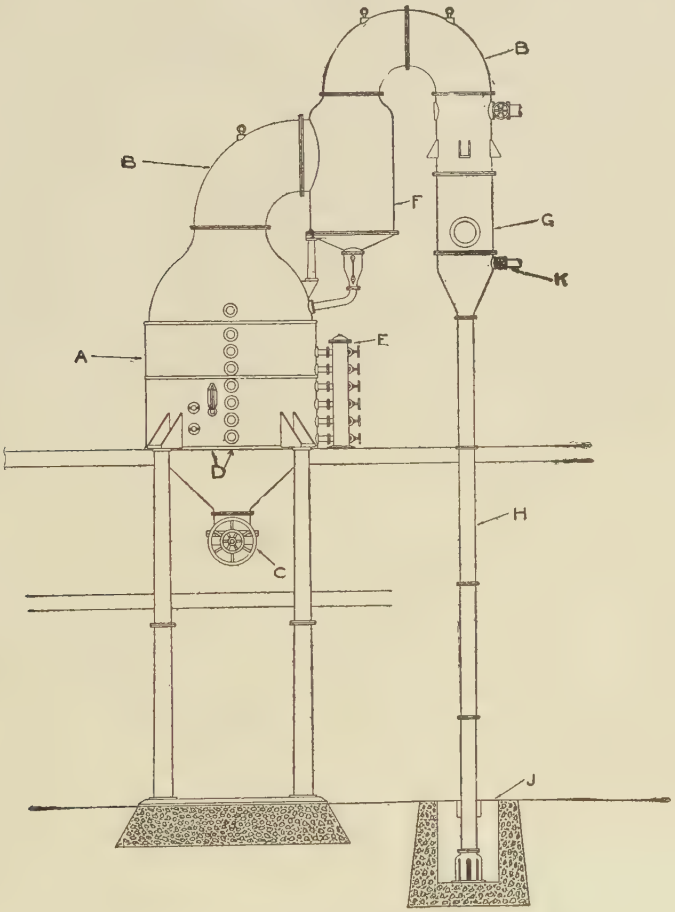

Fig. 340.

ing syrup pass into a condenser, *G*, in which they meet a shower of water. The incondensible gases are lead off through a pipe, *K*, from the lower part of the condenser to a vacuum pump. The condensing water and water of condensation are carried off through the "leg pipe" or torricellian tube, *H*. The foot of the leg pipe is sealed with water, in the hot well, *J*.

The above is a description of the "dry-vacuum system." It is so

called because only the incondensible gases are separately removed by the pump. In the "wet system" the condensing and condensation waters and the gases are carried off by the vacuum pump. The dry system is preferred for large installations. Many factories use a condenser in common for the multiple effects and vacuum pans.

In crystallizing the sugar, the pan boiler proceeds as follows: Having produced a vacuum in the pan he draws in what he deems to be sufficient syrup for graining the "strike," and evaporates it to a saturated sugar solution at the desired temperature. He regulates the boiling-point by the injection of water into the condenser, thus controlling the vacuum. When ready to form the crystals, i.e., grain the strike, he heats the liquor to a temperature of from 60 to 70° C., the grade of sugar desired determining this condition. At this stage there are two customary methods of procedure: In the method usually followed in the cane-sugar factories, the concentration is continued, maintaining a constant or slightly rising temperature, until crystals of sugar begin to appear in the boiling liquor. By means of the proof stick, the pan-boiler withdraws a small sample of the liquid and examines it upon a glass plate by transmitted light. He continues the concentration and these tests until a sufficient number of crystals have separated, dependent upon the grade of sugar he is making, and then admits a small charge of syrup to the pan and frees up the boiling material, being careful not to remelt the almost microscopic crystals nor to cool the liquor sufficiently to cause additional crystals to form.

In the second method of graining, the concentration of the syrup is continued until the appearance of the thread, formed by rapidly separating the thumb and finger moistened with the test sample, shows that the liquor is sufficiently saturated with sugar. The pan-boiler now increases the injection of cold water into the condenser, thus increasing the vacuum and cooling the material in the pan. The boiling mass becomes supersaturated with sugar and minute crystals immediately form. A small charge of syrup is now admitted to the pan and the concentration of the material is so regulated that no more crystals form.

It requires considerable skill in graining to form the requisite number of crystals. If an insufficient number is formed, the crystals will grow large and later in the operation there will not be enough crystal surface, and new grain, "false grain," will form, and the mother liquor will be rich in sugar. False grain impedes the subsequent process of purging the sugar and reduces the yield. Too many crystals result in sugar of too small-sized grain.

After the formation of the crystals the pan-man continues the boiling injecting syrup by charges or continuously if he so elects to compensate for the water evaporated and obtain a saturated solution, but always avoiding temperature and other conditions favorable to further formation of crystals. The charges must be large enough to enable the crystals to circulate freely but not too large in proportion to the crystal surface.

This forces the sugar to deposit upon the crystals already present, which soon grow to the desired size. The material is now concentrated to a solid content of about 92 per cent more or less, and is termed "massecuite." The steam is shut off, air is admitted to the pan, and the "strike" is discharged through the foot-valve into suitable recipients. In making hard-grained sugars a high temperature is maintained until near the end of the operation, and on the contrary, a very high vacuum and low temperatures, produce sugars of low polarization, composed of soft crystals.

In making small-grained sugar, the crystals are formed when the pan is about half filled with concentrated syrup. "Low graining" produces a coarse sugar. If very large crystals are desired, a part of the strike is removed from the pan or is "cut-over" through pipes into an adjoining pan, and the boiling is resumed. If the cut-over pipe is used both pans may be filled with large-grained sugar or one strike may continue with syrup and the other be completed with molasses to form a lower grade massecuite.

The methods described are for liquors rich in sugar and of high purity. In factories using modern methods, the mother liquor or molasses obtained from a sugar of the first crystallization is substituted for syrup, as stated above, to form a "mixed massecuite." Both the massecuite of the first boiling and the mixed massecuite are boiled to definite coefficients of purity, so that the molasses from the last boiling shall contain so little sugar that it cannot be profitably further treated for sugar extraction. In this method the pan work must be supplemented by crystallization in motion in crystallizers such as those described below. In two massecuite work, the first is usually reduced with molasses to a purity of 76° and the mixed massecuite to 60°; in the three-massecuite method, the purities are respectively about 85, 75 and 60°. These conditions vary somewhat according to the grade of sugars.

A crystallizer is a large tank, fitted with powerful mixing arms, and is made in three types, viz., closed crystallizers, open crystallizers, and vacuum crystallizers. The closed crystallizer is a horizontal cylindrical mixing vessel provided with manhole, and charging and discharging connections. The open crystallizer is similar to the closed and differs in having the upper side open, exposing a large area of massecuite to the air. The vacuum crystallizer differs from the closed in having vacuum connections and its lower half steam-jacketed. It is in fact a slow-boiling vacuum pan with forced circulation of the massecuite. The closed and open type are sometimes provided with a water jacket for controlling the temperature, but this is not usual in the cane-sugar industry.

There are many methods of using crystallizers, but a usual one in cane-sugar factories is to boil a strike of mixed massecuite, injecting molasses as described, and running it into the crystallizer. Here the massecuite is constantly stirred during three or four days or until it cools down to the desired temperature. The crystals are kept in constant motion to bring

them into contact with the sugar in solution; thus the sugar deposits upon these crystals instead of forming new ones.

Many factories still simply concentrate the molasses that is rich enough to crystallize, to " string proof," or " blank," and run it into tanks to crystallize at rest. The proof is determined as described in the second method of graining, by separating the thumb and finger moistened with the molasses, thus forming a thread, or more often, the concentrated molasses is poured from the proof stick and the appearance of the " string " formed is noted. The crystals formed at rest are small, soft and of low polariscopic test, whereas those obtained by crystallization in motion are large, firm, and of high test.

Purging and Curing the Sugar. The massecuite, after the completion of the crystallization, is conveyed to mixers from which it is drawn off into centrifugal machines for the separation of the molasses from the crystals.

The centrifugal consists of a shallow drum or basket, having perforated walls and lined with finely perforated brass sheets or brass wire cloth. A customary size for large machines is 40 ins. diameter by 24 ins. depth. By suitable transmission a machine of this size is rotated about 1000 revolutions per minute. A charge of massecuite is run into the centrifugal, usually while the latter is slowly revolving and the speed is then increased until the molasses is thrown off by the centrifugal force and the sugar is retained by the perforated lining.

In making raw sugar for refining, after the above treatment, the crystals are ready for packing and shipment. In the event, however, of the crystals not testing sufficiently near the market basis, 95 per cent or 96 per cent by the polariscope, according to market conditions, after all but the closely adhering molasses has been thrown off by the centrifugal, a little water is sprayed upon the wall of sugar, which quickly removes a part of the low-test molasses from it. Sugars polarizing approximately 96° are termed " centrifugals " and are the basis of market quotations for raw sugar.

Many raw sugars, i.e., sugars that must be refined before they enter into consumption, fall off in polarization during storage. This decomposition is usually attributed to bacterial activity. A loss of 2 to 3 per cent of the sucrose is not unusual during long storage of 96° sugar, and the loss is especially heavy during sea voyages. Certain districts, notably in Java and the Hawaiian Islands, make sugars that polarize above 97° and contain little more than a trace of moisture, since such sugars suffer little decomposition during shipment and storage. Sugars of 96° containing less than 1 per cent of moisture usually retain their initial polarization during storage and shipment. Steam may be injected between the casing and basket of the centrifugal, or into it, to remove the molasses and dry the crystals, or a granulator, as described for white beet sugar, may be used for drying.

In making white sugar in the factory, the juice having been purified as has been described, the crystals are thoroughly washed in the centrifugal with water. Usually a little ultramarine is added to the water " to kill " the yellow tinge of the crystals. A granulator is usually used in drying white sugar. (*See* Beet Sugar.) Superheated steam is also used in a covered centrifugal to dry white sugar. In the latter method the crystals retain their glossy surfaces since they do not rub against one another as in a granulator.

The sugars crystallized at rest from molasses massecuite consist of small, soft crystals, which are sold on a market basis of 89° test or are remelted and reboiled to produce higher grades, or are simply mixed with high-test sugar and sold as such. Crystallizer sugars are often mingled with high purity molasses to form a magma, which is mixed and purged with the first massecuite, thus enabling the factory to produce but one grade of high-test sugar. This method was inaugurated in Cuba by the writer in 1904 and has extended to a large number of factories.

It is customary to " boil-in " molasses on strikes started with syrup or with a " seed " magma and thus produce only one grade of raw sugar. This procedure is modified in white sugar manufacture, in which the low sugar is remelted. The " seed " is a magma formed of low grade, small crystal sugar and syrup or molasses.

The viscous liquid residue after the removal of the crystals, the crystallization having been carried as far as is commercially profitable, is termed " final molasses," or in the markets simply " molasses." With excellent manufacture in Cuba this residue contains about 86 to 88 per cent apparent solids (degree Brix), and 52 per cent of total sugars. This latter consists of about 35 per cent sucrose, by Clerget's method, and the remainder is dextrose and levulose in variable proportions. The molasses contains up to about 9 per cent of ash and has an apparent coefficient of purity of about 30°, i.e., 30 per cent of the solids as indicated by the Brix hydrometer is sucrose by direct polarization. The true coefficient, i.e., that based upon true solids and the sucrose by the Clerget method, is usually above 40° in molasses, made by the defecation process. Molasses by the carbonation process has nearly the same true and apparent coefficients, both very low numbers.

Much lower coefficients of purity may be readily obtained in Louisiana than in the Tropics, owing to the nature of the impurities in the juice. Few tropical factories turn out molasses of lower purity than 30°, or even so low. The average yield of molasses per ton of cane approximates 4 to 6 gallons.

A few Louisiana factories do not attempt to extract more sugar than they can obtain in one crystallization, preferring rather to make a rich molasses of good color that is suitable for the baking industry and the table, the high price of this product more than offsetting the reduced yield of sugar.

The yield of commercial sugar varies with the quality of the cane, the factory equipment and management, and the grade of sugar produced.

The Cuban yield averages a little over 10.5 per cent of the weight of the cane of sugar equivalent to 96° "Centrifugals." A few factories extract as high as 12 to 13 per cent. The Louisiana yield will probably average 7.5 per cent of sugar.

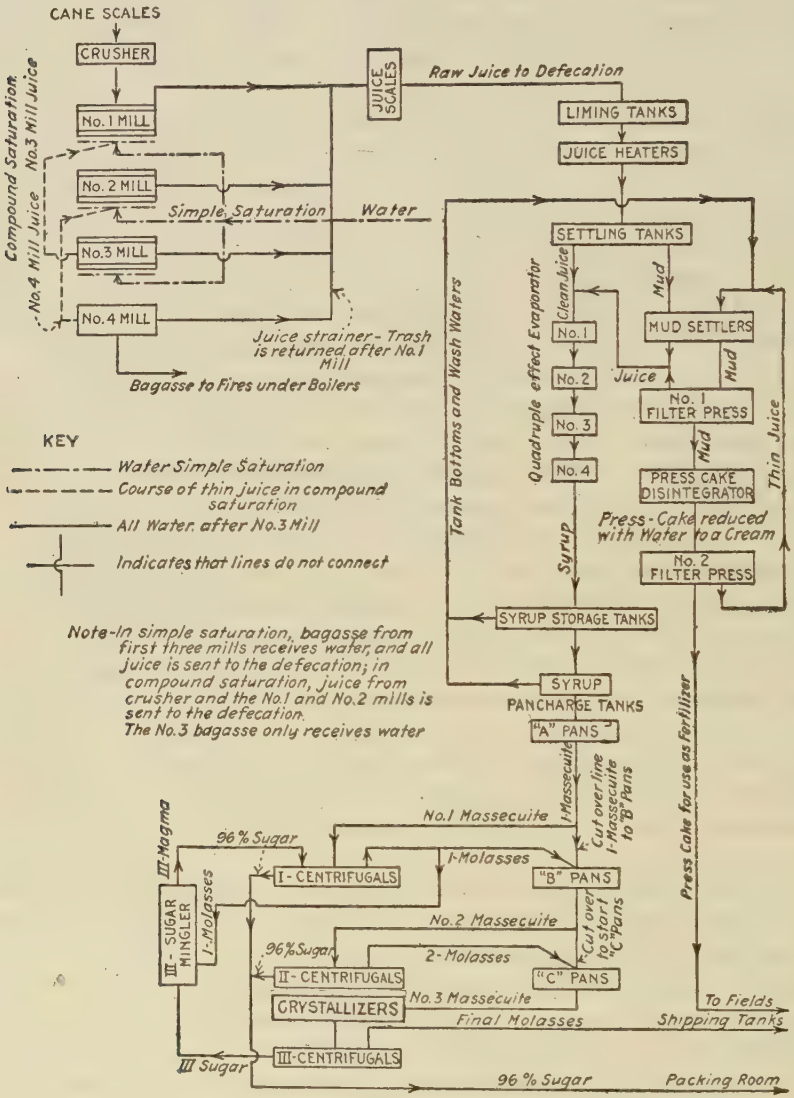

FIG. 341.—Cane-sugar Manufacture. Process Diagram.

The following figures show the average composition of the centrifugal sugars from two very large Cuban factories which produce but one grade of product:

		A	B
Sucrose, direct polarization	per cent	96.64	96.04
Sucrose by Clerget method	"	96.82	96.56
Moisture	"	0.95	1.21
Glucose	"	0.69	1.05
Ash	"	0.63	.32

Factory "A" mingles the third or crystalizer sugar with molasses and uses the magma as "seed"; factory "B" mingles the third sugar and repurges it mixed with first or second massecuite, in both cases producing 96° sugar.

Beet Sugar[1]

Raw Material and its Preparation. The sugar beet is grown from seed. The rows are seeded thickly and the young plants are thinned to leave vigorous ones about 6 ins. apart in the row. The desirable beet is small, the topped root weighing about a pound, and is tapering, somewhat top-shaped, regular in form and has few rootlets. Large beets are not usually as rich as the small ones described.

In addition to the carbohydrates sucrose, raffinose and occasionally slight traces of invert sugar, the following organic substances have been found in sugar beets: Oxalic, formic, citric, malonic, succinic, aconitic, tricarbollicylic, oxycitric, malic and tartaric acids, chlorophyll, betaïne, asparagine, glutamine, leucine, legumine, tyrosine and the xanthine bodies, xanthine, guanine, hypoxanthine, adenine and carnine. The following decomposition products were identified by von Lippmann: Arginine, guanidine, allantonine, vernine, vicine, and in the young plant alloxanthine. The decomposition of these bodies is the source of the ammonia set free in the manufacture and drawn off from the calandrias of the multiple effect. The following non-nitrogenous bodies are also present in the beet: Lecithine, pectose, pectase and coniferine. The mineral constituents include the following substances: salts of potassium, sodium, rubidium, vanadium, calcium, magnesium, iron, and manganese and the following acids in combination with the inorganic constituents: Hydrochloric, sulphuric, nitric, phosphoric and silicic acids. Our knowledge of the composition of the beet is largely due to Scheibler, Schultze and Boshard and von Lippmann. These data are largely from an article by von Lippmann[2] also from Sidersky's *Traité d'Analyse de Matières Sucrées* and Horsin, Deon's *Traité de la Fabrication du Sucre.*

[1] Many of the expressions used in the American beet sugar factories are derived from the German, whereas the corresponding expressions of the cane industry are from the French. The following expressions are examples, that from the German being given first: Thin juice = juice, i.e., juice that has not been concentrated; thick juice = syrup; fill mass = massecuite; wash syrup = wash or washings; green syrup = high-purity molasses, designated by numbers.

[2] *Bul. de l'Assoc. Chimistes de France,* 14, 691, 819.

In preparing the beets for the factory, they are topped at the lowest leaf scar and are then hauled to the factory where they are stored in sheds or in the open upon platforms, according to climatic conditions. When necessary to pile the beets in the field for any length of time, they are protected by a light covering of leaves and earth. Climatic conditions determine the methods of storage. In very cold even climates in the United States very large piles of beets have been successfully stored on open platforms. The frost affects only the outer layers, and as the thawing is gradual the beets are but little damaged.

The beets are flushed to the factory in flumes, waste water being used largely for this purpose. They are elevated to the washing machines by an apparatus which also removes many of the adhering stones and are thoroughly cleansed. From the washing machines they are elevated to automatic scales, above the slicers, for weighing.

Extraction of the Juice. The juice is extracted by the diffusion process. The washed and weighed roots are conveyed to the slicing machines, which cut them into more or less V-shaped slices or cossettes. The slices are packed loosely in the cells of the diffusion battery, which extracts the juice by a somewhat imperfect process of dialysis, the cell walls supplying the membrane.

The diffusion battery consists of a number of cylindrical iron vessels, usually twelve, with suitable pipe connections, heating devices and top and bottom doors. The pipes are so arranged that the liquid may be conducted from one vessel to the next, entering at the top or bottom, at the will of the operator, and permitting any vessel to be disconnected from the series for charging with slices and discharging the spent pulp. A general view of the upper part of a circular diffusion battery is shown in Fig. 342.

In operating the battery, a vessel or diffuser is filled with beet slices, then warm water is turned into it at the bottom connection, driving out the air through a cock in the cover; by the time this diffuser is filled with water, the next one has been charged with beet slices; the direction of the current of liquid in the first is reversed, the water now entering at the top, and the thin juice, as it now is, passes into the second diffuser at the bottom, expelling the air as from the previous vessel. The thin juice is heated in transit and passes into successive diffusers as they are filled with slices. When about ten or eleven vessels have been filled, according to the number in the battery, a measured volume of juice is drawn from the last one filled, the water pressure applied at the first diffuser of the series forcing the juice to circulate. Air pressure is used in many factories, when drawing a charge of juice, to promote economy of water and sugar. The use of water is sometimes preferable, as with it the exhausted pulp may be flushed through canals to the elevators. The spent pulp is elevated to continuous presses in which a large part of its water is expressed. The juice, drawn as described, is strained through depulpers and conducted to tanks for the next stage of the manufacture.

The slices in the first diffuser of the series are now practically exhausted, but 0.15 per cent sucrose, more or less, remaining in them. This vessel is disconnected from the series and the exhausted pulp or cossettes discharged from it.

From now on each time a vessel is charged with beet slices and juice, a measured volume of juice is drawn from it and the spent pulp is removed from the first diffuser of the series, each diffuser in regular order containing the exhausted pulp. The rate of filling the diffusers depends upon their shape, size, the number in the battery and the capacity of the factory. The usual rate of filling is a diffuser of beets every six to seven minutes.

FIG. 342.

The control of the battery temperatures is of the highest importance. The slices must not be overheated or they will mat and impede the circulation of the juice, and, besides, excessive heat favors the extraction of other bodies than sugar; deficient heat results in an imperfect extraction of the sugar. The temperature conditions vary in different factories and also with the quality of the beets. With perfectly sound beets a maximum temperature from 80–84° C. usually gives good results, but the heat must never be sufficient to soften the slices, and must be lower with unsound beets.

The volume of juice to be drawn from each diffuser must be carefully controlled. If too little is drawn the extraction of sugar is imperfect and too much unnecessarily dilutes the juice and causes waste of fuel. The

usual " draw " is from 100 to 110 liters of juice per 100 kilos of beets, the quantity varying with the quality of the beets and the cost of fuel.

As may be seen from the above description, the diffusion process depends upon osmosis, the cell walls of the beet taking the place of the parchment paper in the ordinary process of dialysis. It is therefore very necessary that the knives of the slicers be very sharp, in order that as few cells as possible may be ruptured.

The exhausted pulp is used for stock food. In recent years many factories desiccate the pulp to facilitate shipment to distant markets and to permit of its use as an absorbent of liquid foods, such as molasses.

The yield of desiccated pulp is approximately 5 to 6 per cent of the weight of the beets worked.

Purification of the Juice. The beet juice always contains very fine pulp that passes the strainers of the diffusion battery. This pulp is largely removed by special strainers called " depulpers," and a part of it is carried down with the carbonate of lime in the purification of the juice.

The simple defecation process as applied to cane juice does not give satisfactory results with the beet. In the only process used, the juice is first defecated with lime and then the latter is precipitated with carbonic acid, hence the name " carbonation process " is applied to the method of treatment.

The juice is run into large tanks, where it is limed; milk of lime or quicklime equivalent to about 2 to 2.5 per cent or even more on the weight of the beets of calcium oxide is added. Factories equipped with the Steffen saccharate process for the extraction of the sugar from the molasses, described farther on, use the tribasic saccharate of calcium in part, in liming.

The temperature of the juice during carbonation should be from 70 to 80° C. and may reach 85° with sound beets. Formerly much lower temperatures were advised than are now employed.

The liming is followed by the double or even triple carbonation process. Both the liming and carbonation are usually spoken of as the " carbonation process."

Carbonic acid is forced into the limed juice through distributing pipes. The lime is precipitated as a carbonate and salts of the acids of the juice. The carbonate carries down mechanically many of the impurities that have separated and also much of the coloring matter. The injection of carbonic acid is continued until the juice retains an alkalinity equivalent to about 1 to 1.5 grams of calcium oxide per liter, using phenolphthalein as an indicator. Should this carbonation be carried too far, many of the impurities would again pass into solution. The juice foams considerably during this operation, and steam jets, oil or grease are often used to beat it down. Very deep tanks are used in modern installations to obviate the use of steam, grease, etc. The use of steam is objectionable on account of its decomposing action on the sucrose in the foam.

The workman judges the end point of the first carbonation by the appearance of the precipitate in a test sample of the juice in a spoon. He is also guided by the sound of the bubbles of gas entering the juice. More accurate tests are made by titration with a standard acid.

At the conclusion of this carbonation the juice is heated to near its boiling-point and is then filter-pressed. The filtrate flows into the second carbonation tanks. The juice usually still contains sufficient lime, but in some factories a small quantity, about 0.25 per cent, is added. It is again carbonated, this time at a temperature near 100° C. This is termed the "saturation." The injection of carbonic acid is continued until only slight alkalinity due to lime remains. In determining the end point, the alkalinity due to other alkalis than lime must be taken into account. The usual alkalinity of the saturated juice due to lime is 0.01 per cent or slightly higher.

In a few factories, the second is followed by a third carbonation. In this event a higher alkalinity than stated must be left in the second carbonation. The second or third carbonation is very often followed by saturation with the sulphurous acid gas, derived from burning sulphur. Sulphur is always used in making white sugar. In this case, as before, all but a slight trace of the alkalinity is saturated.

Should too much lime be left in the juice from the last carbonation, the evaporation will be sluggish in the vacuum pan, and the "strike" may even not progress at all. To avoid this difficulty, either the last carbonation of the juice must be pushed farther or the thick juice (syrup) must be carbonated or treated with sulphurous acid. If the syrup is treated with carbonic or sulphurous acid, it must be filtered. These acids are sometimes used simultaneously in the treatment of juice.

Filtration through presses or mechanical filters follows each carbonation and the sulphuring. The filtrate flows to storage tanks preparatory to its concentration.

The chemical reactions involved in the purification of the juice are complicated and not fully known.

The lime neutralizes the organic and inorganic acids and some of these are precipitated, notably oxalic and phosphoric acids; albuminoid matters are partly coagulated and precipitated. Many organic non-sugars, such as albumins, amides, amines and invert-sugar are decomposed; ammonia from the nitrogenous matter and the alkalis sodium and potassium are set free. The carbonate of calcium mechanically carries down the flocculent particles and much of the coloring matter. A little saccharate of lime is often formed, which passes into the filter presscake.

The lime forms soluble salts, many of which persist throughout the manufacture. A part of these lime salts separates during the concentration of the juice to syrup, forming scale on the heating surfaces of the evaporators. These incrustations consist largely of calcium carbonate,

oxalate and a very little sulphate. Iron oxide, alumina and silica from the limestone are also deposited. Considerable organic matter also separates, including undecomposed fat and oil used in beating down foam. Lime soaps form a part of the incrustations. Raw beet sugar usually has a soapy taste and odor. On opening a jar of white beet sugar, a soapy odor may sometimes be noticed.

Evaporation, Crystallization, Purging and Curing the Sugar. These processes and the apparatus used are practically the same as those employed in the cane sugar industry already described.

The American factories usually produce granulated sugar. The granulator is simply a dryer so arranged that the crystals of sugar are separated from one another during the progress of the drying.

The granulator is a long sheet-iron cylinder, placed in a nearly horizontal position and arranged so that it can be revolved. Narrow deflecting plates or shelves are attached to the inside walls of the cylinder and extend throughout its length. The apparatus is inclined slightly toward the discharge end, at which are attached wire screens for sifting the sugar; there is also, at this end, a small room, one wall of which is formed of steam coils. A steam drum extends from end to end of the dryer at its axis. At the inlet end of the apparatus there is a suction fan to draw air through it and a hopper for feeding in the moist sugar. There are several types of dryers, but all depend upon the same principles.

As the sugar leaves the centrifugal machine it is elevated to a mixing floor. It is here thoroughly mixed, since all the pans of sugar and all the centrifugal charges are not of uniform color.

The sugar is next fed into the granulator or dryer, through which a current of hot air is drawn by the suction fan. The crystals are carried upward by the revolving cylinder and in falling from the shelves, through the heated air, are separated and dried. By reason of the inclination of the dryer the sugar travels to the discharge end, where it is classified by the sieves and delivered to the packing spouts.

The yield of sugar from beets, calculated to a raw sugar basis, has reached as high an average as 17 per cent of the weight of the roots in Germany and Austria. The yield is somewhat smaller in the other European countries.

The following is an analysis of a raw beet sugar: Polarization, 94.74; ash, 1.12 per cent; moisture, 1.80 per cent; glucose, none; organic non-sugar, 2.34 per cent. The high ash content as compared with cane sugar should be noted.

Extraction of the Sugar from the Molasses. In the treatment of the beet juice by the methods described, it parts with many of its impurities, yet many remain to impede the crystallization and cause the formation of the viscous after-product, molasses. The molasses from the beet has an apparent coefficient of purity of about 60°, i.e., 60 per cent of its apparent solids (degree Brix) is sucrose. As may be noted in the cane-sugar part

of this chapter, molasses purities below 30° are readily obtained with cane. This difference is due to the nature of the impurities that retard crystallization. Beet molasses contains about 50 per cent of sucrose and but a trace or no dextrose and levulose and about 11 per cent mineral matter, a large part of which consists of melassigenic salts. Cuba-cane molasses, on the contrary, contains much dextrose and levulose, about 25 per cent of

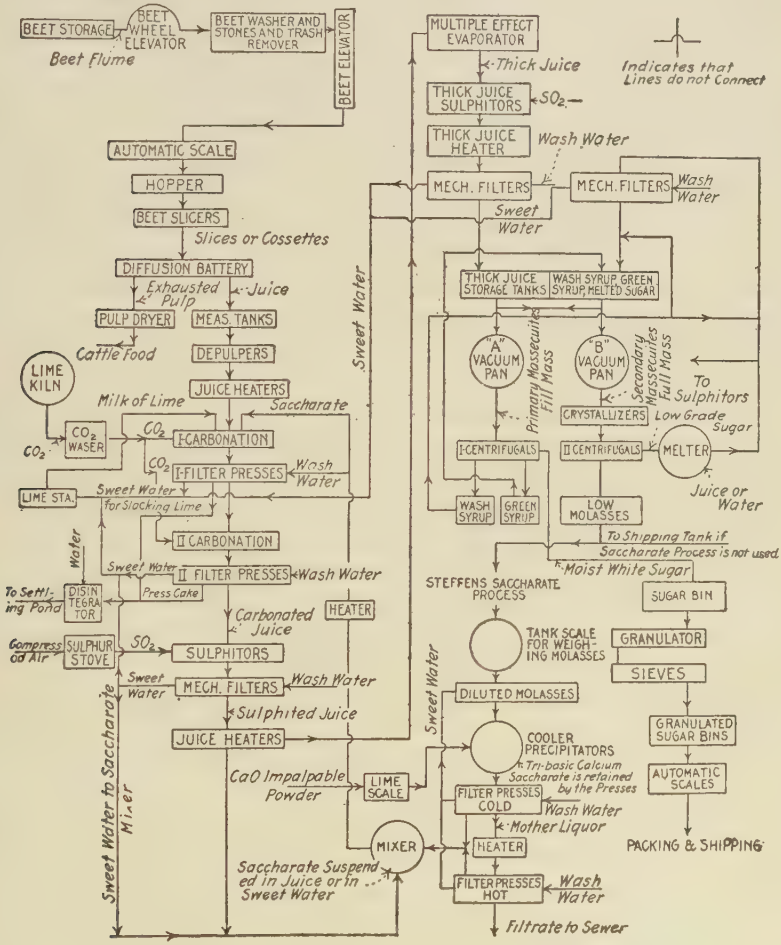

FIG. 343. Beet-sugar Manufacture. Process Diagram.

sucrose, by direct polarization, and upwards of 9.0 per cent mineral matter. Cane molasses obtained by modern methods of manufacture is not usually suitable for table use and does not contain sufficient sugar to justify the installation and operation of plants for the removal of the sugar. Beet molasses is of very disagreeable taste, is rich in sucrose, and the absence of dextrose and levulose makes the extraction of the sugar by precipitation quite simple.

Three molasses processes are now in practical use, viz., osmosis and the strontium and calcium saccharate processes.

The Osmose Process is now little used in the European factories, and has found a limited application in this country. As the name implies, this is a dialytic process.

The molasses is diluted with water to a density varying with its value and the cost of manufacture, and is usually such that the osmosed molasses shall flow from the dialyzer or osmogène at a density of about 35° Brix.

The osmogène has somewhat the appearance of a filter press, and consists of wooden frames separated from one another by parchment paper, thus forming shallow chambers. These chambers have suitable outlets and inlets for water and molasses so arranged that these liquids shall be separated from one another by the parchment. In operating the osmogène, the molasses solution is heated to about 90° C. and the water to 100° C. and these both are circulated through the apparatus. The operation is controlled by the density of the outflowing molasses and that of the water charged with salts and some sugar. The density of the exosmose-water should be about 3 to 5° Brix, this number varying, however, with commercial conditions.

A part of the crystalloids pass through the parchment into the water, including some sugar. Since much of the mineral matter is crystallizable, this largely passes through the parchment, and the saline coefficient of the molasses is very much improved, also its coefficient of purity. The rise in purity permits an additional quantity of sugar to be recovered by crystallization. There is always a molasses residue with this process. Osmosis is sometimes used in conjunction with a saccharate process. The waters are usually run to waste, or may be concentrated and a part of the potash salts recovered by crystallization.

Scheibler's Strontium Process. This process is used in Europe and not at all in this country. The lack of application here is probably due to difficulty in obtaining strontianite and to conditions favorable to the lime and osmosis processes.

In Scheibler's strontium process the actual precipitation and removal of the sugar are readily accomplished, but the necessity of recovering the expensive precipitant makes the process as a whole somewhat complicated.

A solution of strontium hydrate is heated to 65°–70° C. and then sufficient molasses of this temperature to form dibasic strontium saccharate with the strontium present is added with vigorous stirring. The heating is continued to 100° C., with stirring. The dibasic saccharate of strontium is precipitated. The precipitate is collected in filters and washed with a strontia solution. The saccharate is transferred to small crystallizers, where it is cooled to 5°–6° C. and this temperature is maintained until the strontium hydrate crystallizes, leaving the sugar in a solution containing some strontia. The crystals are removed by filtration, washed with a cold solution of the hydrate, and then serve in treating another lot of

molasses. The combined sugar solution and the washings of the crystals are carbonated for the precipitation of the strontium. After filtration the sugar solution is mixed with beet juice in the factory or is concentrated alone for the crystallization of its sugar.

The mother liquor on standing deposits a large part of its strontia. The residue of this, after decantation, is carbonated. The carbonate precipitated in this and the preceding operations, together with the strontia from the mother liquor, are formed into briquettes, and calcined with sufficient strontianite to compensate for the losses. After calcination the oxide is treated with water and the resulting very pure strontium hydrate solution is decanted from the sediment and the salt is recovered by crystallization.

The following chemical reaction is involved in this process:

$$C_{12}H_{22}O_{11}+2Sr(OH)_2=C_{12}H_{22}O_{11}\cdot 2SrO+2H_2O.$$

The monobasic saccharate, $C_{12}H_{22}O_{11}\cdot SrO$, was also used by Scheibler in one of his processes. There have been many modifications of his strontium processes, but in general these relate to the machinery and the methods of recovering the strontia.

Steffen's Lime Process. This method known as the "separation process," in which the sugar is precipitated as a tribasic lime saccharate, is the only one involving precipitation in use in this country. Steffen devised other lime processes, but this is the only one in extensive use.

Steffen's separation process depends upon the precipitation of a granular or crystalline saccharate. He discovered that such a precipitate is formed in the cold. The application of this process therefore involves the use of refrigerating apparatus except where conducted in winter in cold climates.

The precipitant is freshly burned quicklime ground to an impalpable powder. The molasses is diluted to about 12° Brix or 6 to 7 per cent sucrose content in a round mixer, fitted with cooling pipes, mixing arms, thermometer, test cocks, and a measuring device for the lime. The solution is cooled to below 15° C. and then small measured quantities of lime are added to it at intervals or are dusted-in, with very vigorous stirring, the temperature being kept under control and below 15° C. The temperature must be lowered after each addition of lime or with continuous addition of lime; if it rises excessively the rate of adding lime must be reduced. After sufficient lime has been added to precipitate the sugar, with an excess to provide for that hydrated, as is noted by the density of the mother liquor obtained by filtering a test sample, the contents of the mixer are pumped into filter presses, where the precipitate is collected and washed with cold water. The wash water, which carries a little saccharate, is used in diluting subsequent portions of molasses. The filtrate or mother liquor is treated as described below.

The precipitate was at first thought to be tribasic saccharate of calcium $C_{12}H_{22}O_{11} \cdot 3CaO$. The exact composition is apparently unknown.[1] When the writer visited the works at Elsdorf, Germany, to report on this process to the U. S. Department of Agriculture[2] he was informed by the chemist that the washed precipitate contains from 97 to 98 per cent of $C_{12}H_{22}O_{11} \cdot 3CaO$ and that an average of 93.4 lbs. of properly prepared lime powder is required per 100 lbs. sucrose in the molasses. The quantity of lime used depends upon its quality, fineness of the powder, and the temperature maintained in the molasses solution. A too high temperature, coarse powder or too rapid addition of the lime, cause the latter to hydrate in part. Some hydration of the lime cannot be avoided.

The mother liquor from which the tribasic saccharate has been removed contains soluble saccharates (mono- and dibasic) which decompose on heating with precipitation of tribasic saccharate. This solution is heated and the resulting saccharate is collected and washed in filter presses. The filtrate containing some sucrose and nearly all of the impurities of the molasses is run to waste. The saccharate obtained in the first precipitation (" cold cake ") and that from the mother liquor (" hot cake ") are mixed and disintegrated with water and reduced to a cream. This cream is used in liming juice for the carbonation. Prior to such use, it must be heated to near the boiling-point, otherwise the carbonate precipitates upon and occludes particles of the saccharate. Such particles would appear in the presscake and sucrose would be lost.

If the factory treats only its own molasses product, additional lime is necessary for the juice. When the quantity of saccharate is in excess of that required to supply the lime for the carbonation, the surplus is added to a large proportion of hot beet juice and is filter-pressed, or it may be broken up in hot water. Two-thirds of the lime is removed by this treatment, and the filtrate may be used in part in diluting molasses or it may be carbonated, filtered and the filtrate concentrated for the crystallization of the sugar.

Sugars obtained by a saccharate process usually contain notable proportions of raffinose, and the peculiar shape of the crystals often observed is attributed to this sugar. It was at first thought that the raffinose was due to decompositions, but it is now known that it is derived directly from the beet itself.

Residual Molasses from the Cane and Beet. Except where a saccharate process is used there is always a residual molasses from the beet. Cane-sugar factories always produce a final molasses, the average quantity of which is about 4 to 6 gallons per ton of cane in tropical factories making raw sugar. Cane molasses is utilized in rum and alcohol manufacture and in stock feeding. Beet molasses is also used in feeding and in making alcohol. The residue from the distilleries of Europe is concentrated and

[1] " Beet Sugar Manufacture," Claassen, Hall and Rolfe's translation, p. 213; " Beet Sugar Manufacture and Refining," Ware, Vol. II, p. 491.

[2] Bul. 5 Chem. Div. U. S. Dept. Agric.

the organic matter is burned, leaving an ash very rich in potash. Sulphuric acid is added to the mass before burning to reduce the loss of the nitrogen. The ash is used as a fertilizer.

Cane molasses of good color from the manufacture of white and high-grade yellow sugars is used in the baking industry and as a table syrup.

There are many small industries in which molasses is utilized.

Sugar Refining[1]

Raw Material. Most cane-sugar factories make raw sugar testing from 95° to 98° by the polariscope and known commercially as 96° "centrifugal sugar." The Cuban product usually polarizes approximately 96° and that of Java and the Hawaiian Islands up to 98°. Many factories make a lower grade of sugar, a soft sugar crystallized at rest in tanks and testing about 87° and often lower. The market basis for these sugars is 96° and 89° respectively. There is an addition to the price for tests above and a deduction for those below these numbers. The increment of price per degree above these numbers is smaller than the deduction for those below. Similarly the price paid for the sucrose in an 89° sugar is less than that for the sucrose in a 96° sugar. These market conditions discourage the production of sugars much below 96°. Of the sugars imported into New York probably over 80 per cent test above 95°.

A few very small cane-sugar factories do not use vacuum apparatus, but concentrate the juice in open pans until it is saturated with sugar and then run it into coolers to crystallize. This produces a grade of raw sugar termed "muscovado." This name is also applied to certain other grades in Java.

The refining grades of beet-sugar are similar in appearance to the corresponding cane sugars, but have a disagreeable soapy odor and taste. These sugars are high in ash. The buyers make an arbitrary deduction from the direct polarization of beet-sugar to ascertain the "analysis" or "titrage" upon which the price is based. The "analysis" is assumed to be the refining value of the sugar. It is usually determined by deducting five times the percentage of ash from the polarization.

A small proportion of very low-grade sugar, made from a palm and from cane in a crude way, reaches the refineries. Much of this is concrete or juice evaporated to such consistency that it solidifies on cooling.

The average test of the sugars entering an American refinery of the Atlantic Coast is usually between 93° and 95°, the test varying with the refinery and the market conditions.

The invention of the mingling process, described in the next paragraph,

[1] The writer is indebted to Mr. George P. Meade, Superintendent of the Cardenas Refinery, Cuba, for revising the proof of this section and for many suggestions

has greatly facilitated the simultaneous refining of various grades of raw sugars, notably both beet- and cane-sugars. This is accomplished by separating the melt into a high purity liquor and a syrup which carries the larger part of the impurities.

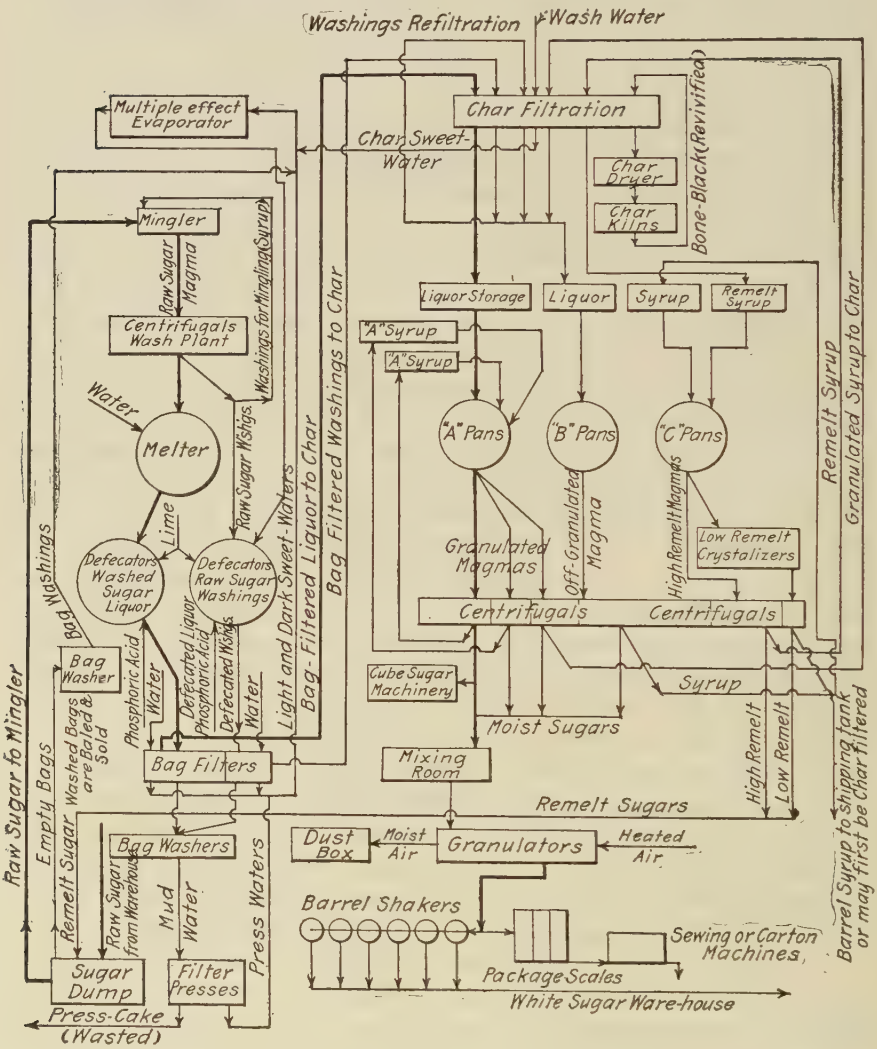

Fig. 344.—Sugar Refining. Process Diagram.

Mingling, Washing and Defecating. The raw sugar is carried by elevators to mingling machines which mix it with syrup and form a magma. This permits spinning the sugar in a centrifugal precisely as though it were a massecuite and thoroughly washing the crystals. This station is termed the "wash plant." The washed sugar is melted with

water to form a liquor of about 60° Brix, and a coefficient of purity of about 98.5° to 99°. The washings or syrup are used in part in mingling raw sugar for subsequent magmas and the remainder is pumped to the defecators or "blow-ups." The blow-ups are provided with perforated pipes through which steam is blown into the liquors.

Sufficient milk of lime is added in the blow-up to render the solutions strongly alkaline and then the alkalinity is neutralized with monocalcic phosphate solution or phosphoric acid. The reagents are used in sufficient quantity to produce a large precipitate that separates sharply from the solution. The filtration is a guide to the quantity of lime to be used. After the addition of the reagents the liquor is heated in the blow-up to a temperature of approximately 82° C.

The refineries often prepare the monocalcic phopshate used in the defecation by treating bone-black dust with hydrochloric acid or the phosphoric acid from dust and sulphuric acid.

Bag Filtration. The warm liquor obtained as above is run into bag or Taylor filters. These filters consist of a large number of heavy twilled cotton cloth bags about six feet long. These bags are attached to nozzles or "bottles" and suspended in a cast-iron chamber. A cotton sleeve of smaller diameter is placed over each bag. This causes the bag to so arrange itself as to give the effect of a fluted filter.

The flocculent precipitate from the defecation consisting of tricalcic phosphate, organic lime salts, gums, etc., and carbon from the bone-black dust, are retained in the bags and a brilliant filtrate flows from them.

The precipitate or "mud" is first washed with hot water while it is still in the bags to partly free it of sugar. After this preliminary washing the bags are taken from the chamber, the mud is removed and they are given a thorough and systematic washing in a series of tubs. The bags are passed through a wringer on their way from tub to tub. The mud and "mud water" are filter-pressed and the filtrate is evaporated with other "sweet water" to a syrup in a multiple effect evaporator. The "thin wash-water" from the bag filters and the washings from the raw sugar packages are evaporated with the press filtrate. Some refineries use a part of these sweet waters in melting washed sugar. It is considered better practice to follow the procedure described. About fifteen hours are required to fill the bags with mud. Sweetland presses are being substituted in part in many refineries for the Taylor filters and for filter presses. Lime and kieselguhr only are then used in the defecation.

Char Filtration. Animal charcoal, bone-black or "char" filters are cylindrical iron cisterns about 10 feet in diameter and 20 feet deep. These are filled with bone charcoal. The char is described farther on.

High-grade bag-filtered sugar liquor, heated to about 71° C., is passed over the char and is followed successively and systematically by granulated syrup, i.e., the run-off syrup obtained in purging sugar to form the "granulated" grade, washings and other low-grade solutions. In making "soft

white " sugars, the liquors are filtered in succession through three filters of char. The liquors flowing from the char are separated into grades according to their color and test. These grades are considered in the vacuum-pan work.

When the char no longer decolorizes the solutions properly, the sugar is washed from it with hot water and is largely recovered. When the purity coefficient of the washings falls too low to admit of profitable treatment for the recovery of the sugar, the water is run to waste. The rich washings are concentrated with other sweet water.

The wet char is discharged from the filters and is dried with the heat of the kilns that would otherwise be wasted. The dried char is heated or " burned " at a dull red heat in tubular retorts in kilns with exclusion of air from the retort. This process is termed the " revivification." The organic impurities of the sugars that have been absorbed during the filtration are burned and the char is returned to filter service in practically as good condition as before use. The char may be used over and over again a great many times, a revivification following each use. The dust is removed by screening and must be compensated for by the addition of from 25 to 50 per cent of new bone-black annually. About 50 to 60 hours are required for a complete cycle of filter operations.

The composition of an American bone-black is approximately as follows: Tricalcic phosphate, 83 per cent; carbon, 10 per cent; calcium carbonate, 4 per cent; calcium sulphate, 0.5 per cent; iron, calcium sulphide, nitrogen and silica in small quantities. The greater part of the char will pass through a 16-mesh screen and be retained by one of 30 meshes.

The filtration of sugar solutions through animal charcoal is primarily for the purpose of removing their color. The char has the further property of absorbing much of the non-sugar of the raw material and thus promotes the crystallization of the sugar. A good char will absorb 85 per cent of the coloring matter, 33 per cent of the inorganic matter and 50 per cent of the organic non-sucrose contained in the raw sugar solution filtered through it.

It may be seen from these descriptions that the char filter station is one that requires skill and a thorough control in its conduct. Errors of judgment here may result in an inferior product and a loss of sugar.

Crystallization and Curing the Sugar. Before considering this stage of the refining a few definitions are necessary: Refiners term a solution from which no sugar has been removed a " liquor," and one from which sugar has been extracted a " syrup." The " syrup " of the raw sugar factory corresponds to the liquor of the refinery and the " molasses " of the factory to the syrup of the refinery.

The crystallization of the sugar is accomplished in vacuum pans in general as described in the raw-sugar section of this chapter. The liquors have a very high initial purity as compared withn the factory syrup and

therefore require repeated crystallization to sufficiently impoverish the final or barrel syrup. The crystals are formed at a high temperature in boiling hard sugars such as granulated, usually above 77° C. This temperature is maintained long enough to produce sharp, clean crystals. In boiling soft sugars, on the contrary, a low pan temperature and very white liquors are essential. A comparatively dark-colored liquor will yield white sugar if the crystallization is conducted at a high temperature, since the crystal will be hard and absorb little coloring matter from the syrup.

The high-grade white liquor is boiled to make granulated sugar, the syrups from this being reboiled with more liquor to make the same grade of sugar as many times as the color will permit. When the color is too dark, the syrup is refiltered through bone-black and, joined with char-filtered raw sugar washings, is reboiled to make "off-color granulated" sugar. The syrups from these last boilings are reboiled to make a raw sugar termed "high remelt" and the syrup from this last sugar, together with the dark-colored liquors from the last runnings of the char filters, is reboiled to make "low remelt" raw sugar. The crystallization of the low remelt sugar is completed in crystallizers as in raw-sugar manufacture.

The methods of pan boiling as above described are typical of a refinery making only hard white sugars. Where soft white and yellow sugars are to be made, the aim is to produce a product of low polarization and good color by combining suitable liquors and syrups and usually boiling the pans at low temperatures.

The sugars are purged of syrup in centrifugal machines. The subsequent stages of manufacture depend upon the grade of sugar that is required. Granulated sugar is cured as has been described for beet sugar, by drying and separating the crystals in a granulator or dryer. Cube sugar is made by molding the moist sugar under pressure and then drying it in an oven. The yellow and soft white sugars are packed while moist, as they leave the centrifugals. Powdered sugar is obtained by grinding very coarse granulated sugar and bolting it through silk bolting cloth. Loaf sugar and tablets are cut or broken from loaves and slabs molded from a magma of white sugar and high-grade white liquor.

There is a very large number of grades of refined sugar, the classification depending upon color, grain, etc.

Barrel Syrup. The residual syrup of the refineries, if of good color, is sold as barrel syrup for baking and table use. If of inferior quality it is marketed for the same purpose as the low-grade molasses of the raw-sugar factories. The syrup is sometimes filtered through bone-black to better fit it for table and bakery uses.

CHAPTER XXXVIII

STARCH, GLUCOSE, DEXTRIN AND GLUTEN

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Starch and Starch Granules. Starch is widely distributed in the tissues of the higher plants, and makes up the larger part of the solids of grains and tubers. When pure, it is a fine white powder having a density of 1.6 and at ordinary temperature is quite insoluble in water, alcohol, ether, or other common solvents. Under the microscope, starch appears as minute, white, translucent grains varying much in size and shape, but so characteristic that it is usually comparatively easy to determine their botanic origin. Morphologically, starch granules can be divided into the following groups:

1. Large oval granules, showing concentric rings and a nucleus or *hilum*, placed eccentrically, such as the various arrowroot and potato starches, the *potato group.*

2. Round or oval granules usually showing the concentric rings and having the hilum irregular, as those from peas, beans and lentils, the so-called *leguminous starches.*

3. Round or oval granules showing hilum in centre. This includes starches from wheat, barley, rye, acorns and many medicinal plants, the so-called *wheat group.*

4. Granules truncated at one end, such as sago, tapioca and cinnamon starches, the so-called *sago group.*

5. Small angular grains, often polygonal, such as maize, rice, buckwheat and pepper starches, the so-called *rice group.*

The size of these granules shows great variation in different starches, being from 0.005 to 0.15 mm. or more.

The structure of the starch granule is quite complex but from the viewpoint of the chemist it can be considered as composed of a colloidal substance, *granulose*, enclosed in an envelope of a more condensed substance of similar composition, *farinose* or *starch cellulose*, the latter making about 2 per cent of the substance of the granule.

If starch is heated to about 70° C., the exact point varying somewhat according to its nature and origin, it *pastes* or swells up into a pasty jelly, the viscosity of which also varies much in different starches. The micro-

scope shows this to be due to the granulose swelling through absorption of water, and bursting the granule. The granules can be gradually ruptured mechanically by grinding starch with sharp sand or in similar ways, or the "cellulose" can be removed by chemical regeants such as dilute solution of caustic alkalies or zinc chloride, when pasting occurs readily in cold water.

Classification. Commercial starches are classified according to their pasting characteristics into *thick-* and *thin-boiling*. The old-fashioned laundry wheat-starch is typical of the first class as a 5 per cent water mixture *pastes* into a thin translucent syrup, scarcely gelatinous at boiling temperature. Corn starch, such as sold for food, when mixed with boiling water in the above proportion, forms a practically non-fluid paste and is characteristic of a *thick-boiling* starch. It is now known that these variations in pasting properties of starch of different kinds are largely dependent on the conditions of manufacture and that thick-boiling starches can be made thin-boiling by suitable treatment.

These properties as well as the degree of gelatinization of the cold paste are of great importance in preparing starches for certain trades. In laundry work and the textile manufactures, for instance, the demand for a paste thin enough to penetrate the fabric when hot without coating the surface and at the same time with *body* enough to give the requisite stiffness make certain types of thin-boiling starches highly desirable. Thin-boiling starches are also used extensively in confectionery. In other industries, as in paper box making, and in certain lines of textile work thick-boiling starches are required.

Sources. Notwithstanding the great variety and wide distribution, there are comparatively few sources of commercial starch. By far the greatest amount manufactured in the United States is made from Indian corn (maize) which averages about 55 per cent starch and of which about 40,000,000 bushels are consumed annually in the manufacture of commercial starches and derived products. Considerable potato starch is also made in this country as well as some wheat starch, the latter being prepared from flour. Tapioca and sago starches are imported to some extent from the far East, the latter used particularly in the manufacture of envelope gums. Cassava starch from Florida and the West Indies has a limited use, and is noted for the body of its paste.

Method of Manufacture. The general principles of starch manufacture are: (1) Disintegrating the plant tissue in such a way that the starch grains are set free but not ruptured. (2) Separating the gluten by diluting with water the disintegrated mixture which has previously been treated with chemicals, or subjected to fermentation, and then settling out the heavy starch by subsidence. (3) Washing the starch by agitating with water in tanks, "running" or decantation. (4) Recovery of the starch by draining in cloth-bottom draining boxes or in deep frame filter-presses. (5) Drying the starch in *kilns*.

Ordinary No. 4 corn which is commonly used in the manufacture of commercial corn starch and its allied products has according to Archbold, the following composition:

	Per Cent
Water	11.60
Ash	1.52
Oil	5.20
Starch	54.80
Other carbohydrates	14.33
Fiber	2.09
Protein	10.46

The corn is shoveled from the railroad cars into conveyors from which it is spouted into the *steep tubs*, which are large wooden vats containing about 2000 bushels. Here it is soaked from two to four days in warm water containing about 0.2 per cent of sulphurous acid. The water is circulated through the corn and by means of an adjoining heating tank is kept at a temperature of 50° C. (120° F). The sulphurous acid seems to have a softening effect on the glutinous parts of the kernel and at the same time prevents undesirable fermentative changes. When the grain is thoroughly softened by the steeping so that the contents of the kernel can be readily disintegrated by moderate pressure, it is usually passed through a Fuss mill. This mill (see Figs. 3 and 4) in its essentials consists of two parallel vertical plates, rapidly revolving in opposite directions and carrying studs which project between each other. The corn dropping between these plates is thoroughly, although not finely broken up. The tough, rubbery germ at the apex of the kernel which contains practically all of the oil, over 30 per cent of its weight, passes out entire, and is separated from the rest of the grain by passing the mass, mixed with an appropriate amount of water, through *germ-separators*, which are tanks containing agitators so constructed that the movement brings the germs to the surface where they are removed by an appropriately placed spout and sieves, the heavier parts of the grain passing off below. The germs are drained and washed from adhering starchy liquor, dried, ground and the oil pressed out of the warm mass by means of oil-presses of the usual construction. This oil is used principally for soap making and for the manufacture of a vulcanized product and in rubber making, although it can be applied to most purposes to which a semi-drying oil can be put. The remaining oil cake is an excellent cattle food.[1] It is ground into meal or shipped in the original cake, the latter, owing to its compactness and unalterability, being particularly adapted for export. The remaining disintegrated grain is mixed with water (liquor, from the separators), reground in a buhr-stone mill (Fig. 7), and the semi-liquid mass passed

[1] Composition of oil cake: moisture, 10 per cent; protein, 22 per cent; starch, 18 per cent; oil, 11 per cent; fiber, 10 per cent; ash, 1.80 per cent.

over the *shakers,* inclined bolting-cloth sieves of about 200 mesh, mounted in a shaking apparatus. The starch with most of the gluten is washed through the bolting-cloth by jets of water or starch liquor, while the woody portions fall off the lower end of the sieve. This process is usually repeated two or three times, the bran after each shaking being passed through roller mills such as are used for grinding flour. The bran or " wet feed " is finally passed through the *slop machine* which wrings out the enclosed liquor and is either sold for cattle feed in this moist state or it may be dried, being often mixed with the gluten meal.

The starch and gluten liquor from the shakers is agitated in tanks to keep the starch in suspension, and its density adjusted to 4–6° Bé. It is then passed over the *runs* or *tables,* which are practically level, the incline being usually only about 4 ins. for troughs 120 ft. long and 2 ft. wide. As the liquid slowly flows down the run, the heavy starch granules, rolling over each other, are practically freed from the adherent coagulated part of the gluten and are deposited upon the bottom, the gluten being carried off the end of the trough. Men with wooden paddles keep the surface of the deposited starch smooth to prevent loss of the starch through any cutting action that might be caused by irregular depositing or accidental obstruction.[1]

The deposited starch which extends in a layer of about 1 ft. thick at the upper end of the run to practically nothing at the foot of the run is shoveled out of the troughs into cars running on a track over the top of the trough and is then dumped into the *breakers.* The breakers are tanks provided with revolving agitators, by means of which the starch may be mixed to a thick cream with water and washed once or twice by decantation according to the quality desired, or it may be purified by revolving again on the tables.

The gluten liquors from the tables always contain considerable starch which cannot be recovered as commercial starch. The liquors, therefore, are settled to remove the excess of water and the residue passed through filter-presses, the cake thus formed being dried, ground, and sold as gluten meal. According to Kaufmann it has the following composition:

	Per Cent
Moisture	9.74
Protein	31.20
Fat	2.35
Carbohydrate	54.67
Fiber	1.44
Ash	0.60

This gluten meal is often mixed with corn bran to form *gluten feed.* The starch milk is either run into *molding boxes,* wooden frames with cloth bottoms, to drain off the water, or filter-presses with deep frames are used.

[1] Recently, mechanical devices, rollers, have been used for this purpose.

Drying Methods. The starch is either dried in trays forming *pearl starch*, or *boxed*, packed tightly in paper-lined boxes, and then the partially dried cake transferred to the drying kiln. The kilns are of various designs. Some are in the form of wooden tunnels through which the cars containing the starch are pushed along by the cars of wet starch entering at one end, the cars of dry starch being taken out at the other. The temperature varies considerably at different parts of the kiln and depends on local factory practice, 160–180° F. being the customary temperature for pearl starch, the drying taking eighteen or twenty hours. Lump starch which is *boxed* is allowed to dry partially at a much lower heat, the blocks turned out of the frames being placed on shelves in a kiln the temperature of which is about 130° F. A yellowish crust which is about $\frac{1}{4}$ in. thick forms on the outside of the blocks; this is removed and the mass of clean, white starch again returned to the kiln where it is dried for several days at a temperature of about 160° F. During this drying the lumps split up into miniature basaltic-like masses technically known as *crystals*. The size of the crystals can be regulated by the temperature; a low heat giving larger and more irregular lumps.

Starch when air dried contains from 12 to 15 per cent of moisture, and if more thoroughly dried in the kilns it will soon absorb water when exposed to the air until the above percentage is reached. The moisture in starch varies also with the humidity of the air; starch dried by heat being one of the most hygroscopic substances known.

Alkaline Starches. The description given above applies specifically to the manufacture of the so-called *neutral*, thick-boiling starches, and in general to corn starch. In making *alkali* starches, caustic soda is added to the starch and gluten liquors before running so as to make the gluten more soluble. Such starches have less nitrogenous impurities but are high in ash, as it is impossible to wash all of the alkali out. Alkaline starches give thicker pastes than neutral starches made by the *sweet* or sulphite processes.

Thin-boiling Starches. *Thin-boiling* starches are made by subjecting the starch to a treatment with very dilute acids at temperatures below the bursting point of the granule, usually 35–50° C. This causes an incipient hydrolysis of the contents of the granule, but does not perceptibly affect the enveloping *starch cellulose*, the dried product being indistinguishable from the original starch, even by careful microscopic examination. A certain very small amount of the granule contents is rendered soluble and can be removed by washing the starch with cold water and filtering. The amount and nature of this soluble carbohydrate, which can be detected by adding a drop or two of a very dilute iodine solution, depends on the extent of the acid modification.

Two general methods of making thin-boiling starches are used in factory practice—the first, known as the *drying in* process, consists in adding either sulphuric or hydrochloric acid in very dilute form, usually

about 1 per cent upon the weight of the crude *green* or *mill* starch as taken from the runs mixed with water. The excess of liquid is then drained off and the starch allowed to dry gradually at a gentle heat. This process has been practically superseded by the *in suspension* process in which case the green starch is dumped into a tank of hot water containing 0.1–0.2 per cent of acid and kept in suspension by means of agitators. When the process is complete, as shown by pasting tests, the acid is neutralized, the starch is drained and then dried in the usual manner. This latter process has been developed largely by Duryea, who has taken out patents. These thin-boiling starches are now made in large quantities, having largely taken the place of wheat starch in the laundry trade.

Potato Starch. Practically all of the starch used in Europe is made from potatoes. Potatoes contain only from 17 to 20 per cent of starch but the actual yield per acre is more than either corn or wheat, for the reason that the potato yield is $6\frac{1}{2}$ tons per acre against about 25 bushels for corn and 31 for wheat, or less than a ton of grain.

The potatoes are soaked in vats of water for several hours and then washed in a long trough containing a spiral stirrer which tosses them about, thus giving a thorough rubbing. Some factories use revolving cylinders for the same purpose. The potatoes are then introduced into rasping machines equipped with rapidly revolving knives; the pulp thus formed being passed through sieves to remove the fiber and the filtrate allowed to settle. The lower layers of white starch are drawn off and the upper gray layers still containing some fiber are resieved and settled, this being repeated several times. The starch is then purified on *runs* and dried in a similar manner to corn starch.

Potato starch is often made thin-boiling by methods analogous to those used in corn starch modifications. Certain patented processes designed to purify the starch by oxidizing the nitrogenous compounds by use of potassium permanganate and other oxidizers also produce thin-boiling modification. Commercial potato starch usually contains about 20 per cent of water.

Wheat Starch. Wheat starch is usually made from flour, either by the old-fashioned method of allowing the mixture of flour and water to ferment in vats and then purifying the starch by settling, in which case the gluten is destroyed by fermentation and a thin-boiling starch results, or by the Martin process in which the gluten is saved and a thick-boiling starch produced. In this latter process, masses of dough made by moistening the flour are placed in a special kneading machine in which the dough is kneaded by grooved rollers working in a swinging frame, the starch being washed out through sieves by jets of water, settled and passed over runs. The resulting starch when dried and finished is thick-boiling and the gluten, still containing several per cent of starch which it is impossible to remove mechanically, is recovered as a rubbery mass.

Rice Starch. Rice starch is made to considerable extent in Europe. There are several processes, but they all depend on destroying the glutinous matter by alkali or fermentation or by both. About 0.3 per cent of potash is usually employed, the steeped grain then being ground and the starch removed by sieving and settling, the last process being a tedious one owing to the minuteness of the granules.

Tapioca and Arrow-root. Cassava (tapioca) and arrow-root starches are made from tubers of tropical plants by processes similar to those used in potato starch manufacture. Certain varieties of the cassava plant contain large amounts of prussic acid. As such starches are used extensively for food, it is necessary that they undergo a special fermentation and washing to remove this poisonous principle. Sago starches are made from the pith of certain palms and are imported both as "flour" and in the form of dry pellets of starch paste. Tapioca is often prepared for the market in a similar way. Cassava starches are noted for the great thickness or body of their pastes.

Commercial Glucose and Other Products of Starch Hydrolysis. Starch, according to Brown and Morris, is a highly condensed hexose carbohydrate of the formula $(C_6H_{10}O_5)_n$ consisting of approximately 100 anhydride groups which can be resolved by suitable hydrolytic agents into as many equivalents of dextrose, providing the hydrolysis is sufficiently prolonged. Dilute acids will produce complete hydrolysis, the rate depending on the nature of the acid and varying approximately as the concentration, but increasing rapidly with rise of temperature. When starch paste is subjected to the action of an acid, it is gradually resolved into simpler carbohydrates, the reaction being the result of the breaking up of the numerous anhydride groups of the complicated starch molecule with the formation of hydroxyl radicles from the water present, the acid not going into the combination, but acting catalytically.

The speed at which this hydrolysis proceeds depends on the amount and nature of the acid and the temperature. If the hydrolysis is carried to completion, the final product is a glucose sugar called dextrose, although in actual practice, some small quantity of decomposition products are usually formed. The intermediate hydrolytic substances are very complicated, but behave chemically and physically as molecular aggregates of three bodies—dextrose, a biose sugar known as maltose, and a dextrin with the properties of the original starch paste.

This progress of the hydrolysis, or *conversion* of starch paste manifests itself by characteristic chemical and physical changes. The thick paste loses its colloidal nature and rapidly becomes more limpid, the concentration of the solution increases, although the dissolved carbohydrates become specifically lighter, and the solution becomes distinctly sweeter in taste. If tested with a weak aqueous solution of iodine, the deep sapphire blue given by the original starch paste changes as the hydrolysis proceeds, passing into violet, then to a rose red which in turn changes to a reddish

brown which grows steadily lighter until just before complete hydrolysis is reached it disappears altogether. A few drops of the solution poured into strong alcohol give a copious white precipitate during the early stages of the conversion; as the hydrolysis continues the amount of precipitate becomes less until near the end when no precipitate is produced.

If the conversion products are tested polariscopically, it will be found that there will be a progressive fall in specific rotation values from that of starch paste (202°) to that of dextrose (52.7°). The Fehling test shows no copper reduction with starch paste, at the beginning of the hydrolysis, but progressively increases till the maximum reducing power is reached when all of the converted products are finally transformed into dextrose.

Since the discovery of the process of converting starch into dextrose by the action of heat and acids, as long ago as the beginning of the last century, dextrose in a crude form and known as *starch sugar* or *grape-sugar* has entered more or less into commerce, but its importance as a product is small as compared to that of glucose which latter has been developed in the past thirty years and become practically indispensable in many food products.

Glucose. The term "glucose" as used to define this product must not be confounded with dextrose or its isomers, but has reference to a special commercial sirup which is always sold under this designation.[1] The name "corn sirup," which has been suggested, would seem to be a happier designation, as is the German "starkezucker Sirop." It is a thick, viscid sirup, practically clear and colorless, or of light amber tint, and is a product of the partial hydrolysis of starch. Its composition varies somewhat but the average product has a specific rotation of about 140°, with a Fehling reducing value of about 47 per cent that of dextrose.

The above corresponds to a composition peculiarly well adapted to the commercial requirements of glucose, which are, that it be a practically "*neutral*" (flavorless) sweet sirup, uncrystallizable when highly concentrated and capable of forming uncrystallizable mixtures with cane sugar when

[1] It is remarkable how few of the apparently well-informed know what "*commercial glucose*" really is. This is due to the confusion of terms which associate this misnamed starch product with grape-sugar and dextrose. It is quite true that dextrose (glucose) is an ingredient of commercial glucose, but the dextrose in the commercial glucose of to-day is the least important ingredient, both in quantity and for the qualities which it imparts to the product.

Pure cane molasses is much more entitled to the name "glucose" than is this starch product so far as its composition and characteristics are concerned. Yet encyclopedias, scientific texts and popular writings are full of erroneous statements confusing "glucose" with dextrose and the glucoses. Indeed, its most earnest advocates and advertisers have been responsible for glaring misstatements both in the public prints and in court testimony through implication of facts relating to dextrose and the glucose sugars to this well-defined product of quite different characteristics. This might not be so surprising except for the tremendous magnitude and importance which the manufacture of this product has in the world's food economy.

the latter is added in large proportion. The sirup also must be capable of being refined so that it is practically colorless. The properties which make glucose valuable in the manufacture of candy, preserves, jellies, sirups and similar food products, are those of a hydrolyzed product which is converted only so far that at least 25 per cent of dextrin still remains in the carbohydrates. If less dextrin is present, the dextrose tends to crystallize out at high concentrations, while it will not adequately prevent *graining* in sugar mixtures. If the conversion is not carried to about this point, the glucose has not the requisite sweetness, while at the same time the preponderance of the less soluble dextrin makes a cloudy, pasty sirup.

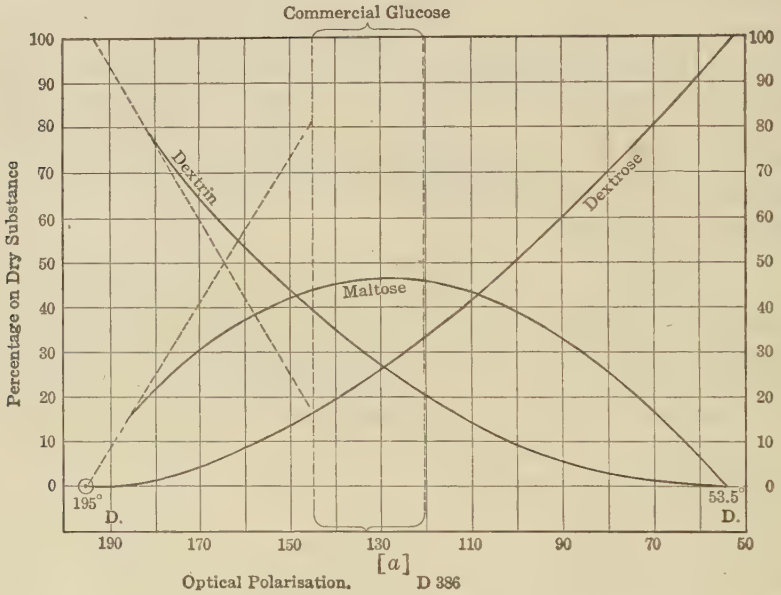


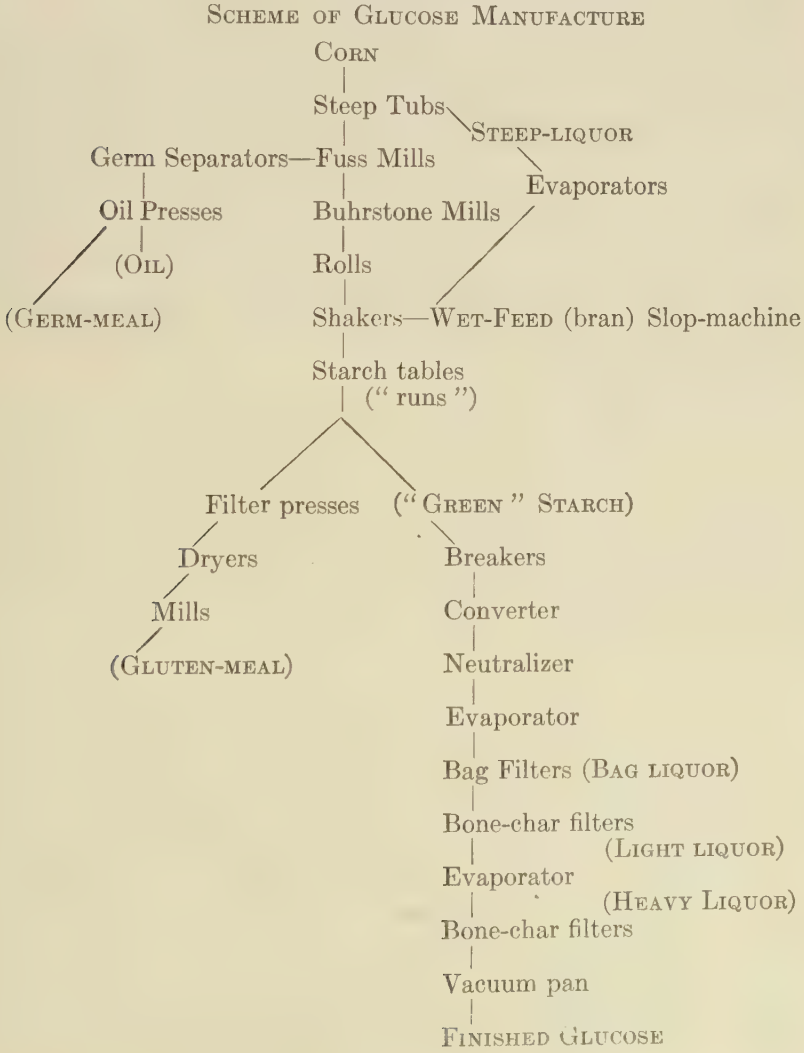
Fig. 345.[1]

A better comprehension of the chemistry of commercial glucose can be had by a study of the following diagram, which gives the variation in percentage of the three primary constituents, dextrin, maltose, and dextrose, present in the carbohydrate matter as acid hydrolysis proceeds, the progress of the hydrolysis being shown by the change in optical rotation from that of starch paste to that of dextrose. The stage of hydrolysis most favorable for the manufacture of commercial

[1] The diagonal dotted lines show the respective dextrin and maltose percentages obtained in starch products hydrolyzed by *diastase* (malt) conversion for the corresponding rotation values. (See "Malt Glucose," p. 779.) These are corrected for the polarization influence of carbohydrates introduced in the malt, which do not come from starch hydrolysis.

glucose for ordinary purposes lies between the rotation values, 120 and 140; although glucose used for special brewing purposes may be somewhat outside these limits. (See Fig. 345.)

Manufacture of Glucose. Glucose is manufactured on a large scale in this country conjointly with starch, gums, dextrins and numerous valuable by-products. Practically all of the commercial product is made from corn (maize), what is known as "No. 4" being usually taken although all grades are used. The following diagram outlines the process and will assist in following the steps, which as far as the production of the *green* (crude) starch are identical with those of corn starch manufacture which has already been described.



Originally, glucose was made in open *converters* which were large tubs provided with steam coils and agitators; but owing to the fact that the speed of hydrolytic action is increased enormously by temperature rise, and as converting at high-pressure effects great economy of time and acid, the open converter has become obsolete. Also, in recent years the pressure has been greatly increased, and the time of conversion reduced by three-quarters or more. Hydrochloric acid is almost universally used as the hydrolyte owing to its greater converting power and because it gives a brighter, more easily refined product.

The green starch is taken directly from the tables to the converter being shoveled off the runs, and mixed with water in a *breaker*, a tank with an agitator, to a thick cream usually standing about 20° Bé.

Horizontal Converter. The older type of converter, which is still in use, is a horizontal cylinder usually made of gun metal or copper. The diluted acid is introduced, steam is then turned on and a pressure of about 30 lbs. maintained. The starch liquor is then gradually pumped into the converter in a fine stream, twenty minutes or half an hour being consumed for filling. This allows time enough to permit the entering starch to become sufficiently hydrolyzed, to prevent pasting; otherwise, large clots would be formed, plugging the apparatus and causing *freezing*. The conversion is then continued under pressure of about 30 lbs. until iodine tests made on small samples withdrawn from the apparatus show that the proper conversion point has been reached, which usually takes from fifty minutes to an hour.

Vertical Converter. In the more modern type of converter, which is similar in construction but vertical, the starch milk is mixed with part of the acid before introducing into the apparatus and is thus partially hydrolyzed in a separate tank, a larger proportion of acid being used. The whole charge is run in a few minutes into the hot converter through a large opening in the top, the cover immediately screwed on and the steam pressure quickly raised to about 50 lbs. Owing to this high pressure and the greater strength of acid used the starch is almost immediately liquefied, thus causing the whole conversion to be completed in about ten minutes.

The converted liquor is turbid from the colloidal albuminoids it contains and has a density of about 16° Bé. It is immediately blown out of the converter into the *neutralizer* which is usually a large covered wooden tank provided with a stirrer and also having ventilating shafts for the removal of hot vapors. Here it is treated with a dilute solution of sodium carbonate which not only neutralizes the acid, but at the same time coagulates the colloidal albuminoids and precipitates the dissolved iron so that a bright filtrate is obtained.

From the neutralizer, the liquor goes to bag-filters of the type used in sugar refining (Taylor filters). The practically clear amber-colored *bag-liquor* usually goes thence to the bone-char filters for its first decolor-

ization, but often it is first subjected to a further treatment with precipitants and filter-pressed before going to the bone-char.

Char Filters. The bone-char filters are identical with those used in sugar refining, being vertical cast-iron cylinders containing 20 tons or more of char, but greater care has to be taken in the preparation of the char and in the filtering since all those impurities which affect the color, appearance, flavor and give other objectional qualities must be removed at this stage, if at all, as they cannot be collected in the mother-liquor by crystallization as in cane-sugar refining.

Since the slightest trace of caustic lime or other alkali in the char will cause a brown coloration in the hot liquor, it is necessary to subject the char in the filters to a careful preparation known as *tempering*. This consists in a treatment with dilute hydrochloric acid, washing with hot soft water and a partial drying by means of steam or compressed air. This neutralizes the alkali which is present consisting principally of caustic lime and ammonia and also removes considerable of the soluble salts, especially those of iron.

The glucose is passed twice through the bone-char filters, the first passage follows bag-filtering resulting in what is known as *light liquor*. This liquor is evaporated in a multiple-effect apparatus to a density of about 30° Bé., and again goes to the bone-char filters, when the product is known as *heavy liquor*. The method of procedure is as follows: The fresh bone-char as it comes from the kilns is cleaned from the dust and smaller particles which would cause clogging of the filters. It is then spouted in through a manhole until the filter is filled to within 2 or 3 ft. of the top. The hot tempering acid is then added until the char is covered, and is allowed to remain in contact with it for some time. The acid water is then drained out of the bottom of the filter and the wash water introduced, which is also drained out at the bottom. The drainings are then blown out with steam or compressed air. The filter is now filled with hot, heavy liquor which is allowed to stand for some time in contact with the char. The liquor is then slowly displaced by more heavy liquor entering at the top of the filter, the filtered liquor passing out through the bottom by means of a pipe which rises nearly to the top of the filter, thus keeping a constant level just over the upper surface of the char.

After the heavy liquor has been running over the char continuously for four or five hours, the time depending on the working of the filter and other factory conditions, the last filter full is displaced by the light liquor which then runs through the filter in the same manner for several hours. By the end of this time the capacity of the filter for efficient work has been reached, and it is now *sweetened off* by displacing the light liquor which remains in the filter by soft water, continuing the flow till a Baumé-spindle test at the exit pipe shows that all the liquor has passed. These "sweet waters," together with the washings of the bag-filters are concentrated in an evaporator and usually put into the bag-liquors. The filter

is now washed for a number of hours by a reverse flow of hot, soft water, the water entering at the bottom and passing out at the top of the filter. After this washing the char is dumped through a manhole in the side at the bottom of the filter and is carried by conveying machinery to the kilns where it is dried by passing over hot flues in the upper part of the kiln and then heated to dull red as it passes through the tubular iron retorts. These tubes are placed vertically in the kiln and are connected to sheet-iron tubes extending out through the bottom of the kiln which serve to cool the char. The retorts and coolers are kept entirely filled with the char which is made to pass through them very slowly, at regular intervals, the char being removed in small quantities from the bottom of the coolers. In this way a large part of the organic matter which clogs the pores of the char is volatilized or destroyed without injuring the char itself. After passing through the kilns and sifted, the char is again ready for the filters. There is necessarily some loss in this *revivifying*, 1 per cent or more being removed by the sieves in a state too fine for use in the filters. This *spent char* is of considerable value, however, as it is used in the manufacture of fertilizers, colors, and for other purposes.

Concentration. The practically colorless heavy liquor coming from the bone-char filters is now ready for the final boiling down in the vacuum-pans whence it comes as finished glucose and is run into the barrels for shipment.

As glucose liquors, even in the vacuum-pan, will color somewhat when boiled to the concentrations required of the commercial product, it has been the practice to inject a solution of acid sodium sulphite (*bisulphite*) for the purpose of bleaching during concentrating in the vacuum-pan. The bisulphite also acts as a preservative of the thinner sirups in which glucose was used. It further prevents, to a great extent, its darkening in the kettle, when used in hard candy manufacture. Since the enforcement of the Pure Food Law in this country in 1907 use of sulphite in any appreciable amount has been forbidden in glucose for food,[1] so glucose made since the enforcement of this law has had a light amber color.

All refined glucose contains to a greater or less extent, depending on the quality of the refining, certain impurities which cause objectionable color, flavor and odor, present it is true, in very small quantity, but still significant as affecting the value of glucose for many purposes. It is now known that these are actually impurities and not inherent in the carbohydrate, being in the main nitrogenous decomposition products from the small quantities of gluten left in the starch and resulting from its acid hydrolysis in the converter. The effect of these objectionable impurities, particularly the color, has been mitigated by the use of sulphites, which, more or less temporarily, bleach the goods and also mask to some extent the objectionable odors and flavors. Now that the use of sulphites is pro-

[1] Temporarily pending investigation of this matter the government has waived prosecution for the use of sulphurous acid compounds in sirups up to 0.035 per cent.

hibited in glucose used as a food, manufacturers have been obliged to use starch which has been especially purified by washing or rerunning on the tables. Rerun alkali-process starches have been used, giving a somewhat better product but they have the disadvantage of increasing the mineral content of the product, owing to the alkali introduced which cannot be completely removed and also because of the greater amount of hydrolyzing acid required.

Duryea has patents for manufacturing glucose from a pure modified starch in which the purification is accomplished by a mild acid hydrolysis and subsequent removal of the hydrolyzed impurities by the usual methods, such as washing or rerunning.

Glucose is usually made at three concentrations, 42°, 43° or 45° Bé., and, as has already been stated, as a rule, is converted to a point represented by a specific rotation for the anhydrous carbohydrate of about 140° D. Apparently, there is no attempt to vary the composition of the product for special trade uses as could easily be done to advantage, but the lighter-colored pure glucoses are selected for confectioners' use, irrespective of the degree of conversion. Glucose used for the manufacture of table sirups is usually known as *mixing glucose*. Such sirups are made from cane sirups, usually refinery molasses, or from white sugar and glucose in the proportion of 85 per cent of glucose to 15 per cent of cane sirup. Table salt and sometimes small quantities of vanillin are often added. The other principal uses of glucose are in the manufacture of jellies, preserves and in brewing, although its applications are multifarious in many industries where it does not enter as a food product, as for instance, it is used in enormous quantities to fill sole leather and tanning extracts.

Grape-sugar. Grape-sugar is the name applied to a crude dextrose which is manufactured in considerable quantities in this country and is used chiefly in the manufacture of vinegar and in brewing, also as a reducing agent in many industries, as in indigo dyeing, and in silvering on glass. It contains from 70 to 80 per cent of dextrose, the balance of carbohydrates being those of the lower hydrolyzed products. Grape-sugar is not much used in food products owing to its bitter, unpleasant flavor, largely due to the effect of the greater degree of hydrolysis on the nitrogenous impurities of the starch already referred to and also to the decomposition products arising from the prolonged action of the acid and heat on the carbohydrate itself. The initial steps of grape-sugar manufacture are the same as those of making glucose, except that more hydrolyzing acid is used, and the conversion is carried to the point that no dextrin is precipitated when the sample is poured into strong alcohol.

As it appears in the market, grape-sugar is a hard, waxy solid, being in the main in the form of *concrete* compact masses of crystal plates of the crude dextrose monohydrate, made by pouring the highly concentrated liquors into molds. When fresh, it is usually quite white, especially when bleached with sulphite, but it darkens with age, and the

lumps become very hard. Two grades of this quality of grape-sugar are on the market, known respectively as *seventy* and *eighty* sugar, the figures being supposed to represent the per cent of dextrose in the goods.

About 1880, Dr. Behr invented a process for making anhydrous dextrose in a commercial way, and this sugar is now made to some extent. The process consists in starting a crystallization in aqueous solutions of commercial dextrose, under favorable conditions of temperature and concentration, with *seed* or pure anhydride obtained by crystallization from alcohol. The anhydride thus obtained is in fine needles which are practically chemically pure, and can readily be purged from the mother-liquors, from which the darker, "*Climax*," sugars are made for brewing purposes.

Malt-glucose. In Japan, glucose has been made for centuries by primitive methods of converting the starch of rice and millet. *Midzu-ame*, as it is called, in its better grades, is a light yellow transparent sirup resembling our commercial glucose, and by analysis it is shown to be a practically pure diastase-converted starch product. In Europe, similar sirups have been made to some extent, and practically unrefined sirups made from ground malt and other grains, known as *malt-extracts*, are common pharmaceutical preparations in this country. Commercial glucose made by use of malt has not yet been put on the market as a regular product of starch. One reason for this has been the relatively large amounts of malt necessary for conversion which made the cost of production prohibitive. In 1903, Duryea took out patents for an improved method of making malt-converted glucose, called by him "maltose" in which the process starts with a purified starch, which is subjected to an acid hydrolysis of short duration before the malt infusion is applied. In this way a very small amount of malt extract is required and a conversion obtained which gives a product practically identical with that obtained from a normal disastase conversion, but very small quantities of dextrose being present.

A "maltose" thus made is odorless and practically free from flavor, the objectionable nitrogenous by-products formed by acid hydrolysis apparently not being produced in this method of conversion.

Dextrin and British Gum. Artificial gum made from starch and known as *dextrins* and *British gums* are made in large quantities both in this country and Europe, and are employed in many ways as substitutes for natural gums such as tragacanth or gum arabic. Enormous quantities of these starch gums are used in the textile industries, for envelopes and postage stamps. These products are made by heating (*roasting*) starch in revolving cylinders, which are heated directly by a furnace or by an oil-bath, or in shallow trays in shelf kilns. The temperatures used vary much according to the product desired, varying from 170 to 270° C. In making dextrins, lower temperatures are used and the starch is moistened with dilute acid, usually nitric, 0.12 per cent, previously to heating so that

in the earlier stages of heating, considerable hydrolysis takes place. In making British gums usually no acid is used, but the temperature employed is higher, and even in this process hydrolysis first takes place to some extent, owing to the moisture and acid naturally in the starch. The time of heating varies much according to the product, white dextrins taking but two hours, while British gums are heated for fifteen hours or even longer. There are no exact standards for dextrins generally recognized, color and body of the mucilages which measured quantities of these gums make are usually the best means of their valuation. These products are not definite chemical compounds, neither are they made according to fixed methods of procedure. Often different products are blended to give the properties desired. Little is known of the chemical constitution of these products, however much has been assumed. They contain some products of acid hydrolysis, it is true, but they are not in the main identical with products of acid hydrolysis.

Soluble Starch. Soluble starch is starch which has been but lightly dextrinized, and is practically identical with many so-called white dextrins. Actually there is no exact limit in the hydrolytic stages between soluble starch or dextrin and thin-boiling starches, as certain of the higher converted thin-boiling starches contain considerable substance more or less soluble in cold water, but there is an exact practical distinction. Soluble starch disintegrates in cold water into a smooth colloidal paste, whereas thin-boiling starch immersed in cold water preserves the form of its granules unchanged, and when dried at temperatures which do not affect the granules, preserves its original appearance.

So, too, it is usually impossible to subject commercial starch to any action of washing or other treatment with water or heat without subjecting it to more or less incipient hydrolysis which can be recognizable by appropriate physical or chemical tests.[1] Hence, as already stated, most commercial starches show certain evidences of hydrolysis usually incipient, it is true, and dependent on the method of manufacture. At the same time there is a clear distinction between what is known in the trade as *thick-boiling*, *thin-boiling* and *soluble* starches which is based on the behavior of these products under various tests of their properties as applied in the industries.

Oxidized Starches. Beginning with 1894, Siemens and Witt, in Germany and England, patented methods for purifying potato starch by means of various oxidizing agents, chlorine, potassium permanganate and the like. It was noted by the patentees that the starch was modified so as to be what is now termed "thin-boiling." Of recent years a number of patents have been taken out for starches, mainly for adhesive and sizing purposes, in which chlorine, chloric and perchloric acids, and other oxidizers have been used for modification, alkalies and alkaline earths

[1] However, absolutely *fresh* starch when washed or rerun and quickly dried before fermentation change can occur is made *thicker* boiling, probably due to the purification.

being used to increase the adhesive properties. Perhaps the most important of these processes is that of Perkins, in which cassava starch is modified with sodium peroxide and caustic soda. (U. S. P. 1,020,655 (1912) Reissue 13,436.) This product is sold in the dry form as a peroxide-modified starch which is to be pasted with caustic soda and 2 to 3 parts of water according to the patented formula. It is used extensively as a successful glue substitute, particularly in veneering.

Gluten. The protein matter known as "gluten," which forms the largest proportion of the organic material associated with starch, is necessarily removed or destroyed in the process of starch manufacture. By the more modern processes the gluten is saved and formerly these semi-liquid gluten desposits were sold to the neighboring farmers for immediate feeding to their cattle. Now, as has been already stated, in the manufacture of corn starch the gluten which is settled out of the liquor coming from the starch runs is filtered in filter-presses, and the cake dried and pulverized, making a valuable cattle food especially when mixed with the corn bran or similar material.

In wheat-starch manufacture, by the Martin process, the gluten, which is obtained in large rubbery masses, is similar in many of its chemical and physical characteristics to blood albumen, and when properly prepared can be used as a substitute for the latter in calico printing. It also has been used in the manufacture of adhesives, as has corn gluten to a limited extent. Gluten foods have also been made from wheat gluten, these being in demand by physicians where non-starchy vegetable foods are indicated, but the difficulty has been to obtain the gluten even approximately free from starch as it is impossible to do this by mechanical means. Hence, most of these so-called gluten foods have been far from satisfactory when starch-free products are required. The only successful method of removing the starch has been by hydrolyzing with malt, at comparatively low temperatures and washing, but such products, while on the market, are too expensive for general use.

Corn gluten, as usually produced, is not a palatable food for mankind, but if suitable care were taken with this by-product throughout the process with a view to this end it would seem as if a valuable "*breakfast*" food might be made.

The perishable nature of all gluten, which demands prompt and careful drying to preserve it, and its sensitiveness to only moderately high temperature, make it difficult to work up and store.

Wheat gluten from its close resemblance to albumen has been much more developed in its industrial applications, but the supply of this is too limited for its extended use.

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CHAPTER XXXIX

BREWING AND MALTING

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Brewing is the process of preparing hopped, fermented beverages, such as lager beer, ale, stout, weiss beer, the materials usually employed being barley-malt, hops, and water.

Malting is the process of preparing cereals, usually barley, through germination, for purposes of conversion and fermentation.

Prehistoric. One of the earliest fermented beverages known to tradition, *mead,* was prepared from honey-water, that is, the washings of honey combs; hence, according to Arnold, the Latin designation for beer, "Cerevisia" originated from the Celtic Keirwysg (Keir = wax; Wysg = water), and not from Ceres = cereals and vis = vigor; "this word was simply retained after cereals were used with the honey and even after cereals were used alone." [1]

What Beer was and is.[2] There is no legally fixed definition of the article or term "beer"; its manufacture and sale come under the provisions of the United States Food and Drugs Act of 1906, where it is classed as a "food." National and State committees and associations on food standards have wrestled with the problem of what beer is, long and often, but their labors to propose a satisfactory standard have thus far been fruitless, and all beer standards have therefore remained tentative ones up to the present time.

Beer of Old—Norse, Teutons, Germans. From ancient times down to the present, the popular beverage that passed by the name of beer has been undergoing so many changes as to material employed, qualitatively and quantitatively, equipment, processes of manufacture and character of product, that it is impossible to fix a standard from usage alone that will not allow the widest latitude as to choice of materials or processes. With the older Norse and South Teutonic, or Germanic tribes, beer was a tart fermented beverage in which honey was a prominent constituent, and about the eleventh century the employment of hops became general on the Continent because of its bitter and aromatic and antiseptic principles and tonic effect. Later this ingredient became universal.

[1] J. P. Arnold, "Origin and History of Beer and Brewing," Chicago, 1911.

[2] Address before the Second International Brewers' Congress, Chicago, Ill., Oct. 18–21, 1911.

Cereal Base. As to cereal base, barley undoubtedly took the lead from the first, as it was the great staple article of food before wheat displaced it in breadmaking. But other cereals have had their importance in beer-making in ancient as well as modern times. So China made its beer 3000 years before the Christian era from rice and millet besides barley, and in Egypt, probably as early as the building of the pyramids, millet was employed along with barley. In modern times, the variety of cereals used is much the same. In many countries, notably the United States and Great Britain, unmalted cereals like rice and corn are generally employed and sugars are favored by some; in Germany wheat is employed for some beers, and in France, Belgium and Scandinavian countries various cereal products besides barley malt, such additions to barley malt in these countries being made to secure, especially, better keeping quality and to tone down the satiating effect or richness of all- alt beverages.

The idea that the only pure beer is an all-malt beer is thus seen to be false, both actually and historically, and beer may therefore be defined as follows:

"*Beer is an effervescent beverage resulting from the thorough alcoholic fermentation of a hopped solution, in potable water, of the extractive substances principally of barley malt, together with, if desired, other prepared cereals or their natural equivalents.*" [1]

Technically, beer is an effervescent beverage properly brewed from sound materials, principally barley malt and, if desired, other prepared cereals or their equivalents; hops and potable water; with the resulting brew or wort thoroughly fermented by yeast.

Chemically, beer is an effervescent fermented malt beverage, containing in aqueous solution the products of thorough fermentation by culture yeast, mainly alcohol and carbonic acid, and a residuum of unfermented extractive substances, like dextrins, maltodextrins, maltose, albuminoids, acid phosphate, lactic acid, extracted from barley malt or other prepared cereals or their equivalents; hop bitter acids from hops; mineral constituents from the water, and the aromatic principles from hops, malt or fermentation.

Dietetically, beer is an effervescent, zest-giving, fermented malt beverage of nutrient and tonic value.

Hygienically, beer is an effervescent, refreshing, fermented malt beverage, biologically sound or wholesome, that is, devoid of, and offering resistance to the development of, pathogenic or virulent microbes of all kinds.

Economically, beer is one of the greatest industrial products of many of the foremost nations. America produced during the last year over 65,000,000 barrels of beer, representing a market value of about

[1] Address before the Second International Brewers' Congress, Chicago, Ill., Oct. 18–21, 1911.

$400,000,000, and providing a revenue to the government of approximately $65,000,000 for the year.

Technically, lager beer is an effervescent sparkling beverage, properly brewed from sound materials, principally barley malt with, if desired, prepared cereals like corn or rice or their equivalents; hops and potable water; with the resulting brew or wort thoroughly fermented by culture bottom yeast and the fermented product stored in refrigerated cellars for sedimentation; clarified, if desired, by filtration, and properly sterilized, when bottled, by pasteurization.[1]

The uniform standard for *malt liquors* tentatively adopted by a Joint Committee on Food Standards, representing the Association of Official Agricultural Chemists, and the Association of State and National Food and Dairy Departments, at a session at Mackinac Island, on August 3, 1908, is:

"Malt liquor is a beverage made by the alcoholic fermentation of an infusion, in potable water, of barley-malt and hops, with or without unmalted grains, decorticated and degerminated grains."[2]

Character and Properties of Beer. Before selecting and weighing the materials in order to start brewing operations, the brewer should clearly understand the requirements the finished product is to meet, and every operation he carries out should be understood with a knowledge of the influence it may have in shaping the character of the beer as desired.

A beer has *quality* if it possesses recognized merit and meets the requirements of the trade.

A beer has *character* if its properties conform to those of a recognized standard or type.

Typical beers may differ widely as to their distinctive properties. We may distinguish, for instance:

The *Bavarian* type of lager beer, with a light brown to dark brown color, malt flavor, and a sweetish taste as the main features, with the aroma and bitter taste of hops but little pronounced; usually lively and sparkling. Alcohol content about $3\frac{1}{2}$ to 4 per cent. From worts of about $12\frac{1}{2}$ to $14\frac{1}{2}$ per cent extract.

The *Bohemian* type of lager beer, with a light yellow to greenish yellow color, pronounced hop aroma, and bitter taste; while the malt flavor is not pronounced; usually lively and sparkling. Alcohol content about $3\frac{1}{2}$ to $3\frac{3}{4}$ per cent. From worts of about $12\frac{1}{2}$ per cent extract.

The *Vienna* type of lager beer, with less pronounced character than either Bavarian or Bohemian types; in point of color, hop, and malt aroma, sweet and bitter taste, it takes a place between these two types. Alcohol content about $3\frac{3}{4}$ per cent. From worts of about $13\frac{1}{2}$ per cent extract.

[1] Address before the Second International Brewers' Congress, Chicago, Ill., Oct. 18–21, 1911.

[2] Wahl-Henius "American Handy-book of the Brewing, Malting, and Auxiliary Trades," 1908, p. 1443.

The *Dortmunder* type of lager beer, with very light color; from long-grown, low kiln-dried malt, hop and malt flavor not very pronounced; highly and completely attenuated. Alcohol content about 4 to $4\frac{1}{2}$ per cent. From worts usually above 14 per cent extract.

The *American* type of lager beer, with a light color, and pronounced hop aroma, less bitter than the Bohemian, with a high degree of brilliancy; quite lively and sparkling. Alcohol content about $3\frac{1}{2}$ to 4 per cent. From worts of about 11 to 14 per cent extract.

Ale, with a light color, very pronounced hop aroma, and bitter taste, and with a rather high percentage of alcohol and tart taste in the aged product, either lively or still, and usually clear. From worts of about 14 to 16 per cent extract.

Stout, with a very dark color, malt flavor and sweet taste, brewed stronger than ale, and possessing a tart taste in the aged product, but less alcohol than ale; usually lively. From worts of about 16 to 18 per cent extract.

Porter, with a dark color, brewed like stout, but not so strong.

Weiss Beer, very light in color, no pronounced malt or hop flavor, quite tart, very lively, but not usually sparkling; often turbid.

Common and *Steam Beer*, light in color, hop aroma and bitter taste not very pronounced; very lively and not necessarily brilliant.

All so-called lager beers, like the American, Bohemian and Bavarian types, should possess a certain degree of palatefulness, and should draw with a creamy, lasting head, which requirements are not to the same extent to be met by the other brands.

Besides the above there are brewed in America beers or beer-like beverages to meet special requirements, for instance:

Low-alcohol Beers, less than 2 per cent alcohol by volume.

Tax-free beverages whether beer-like or not, 5 per cent alcohol by volume.

Non-alcoholic beverages whether beer-like or not, less than .1 per cent alcohol by volume.

Tonics, so-called: bottled, and brewed with a high percentage of extract, usually all-malt beers, possessing a dark color, either thoroughly fermented with a high percentage of alcohol and comparatively low percentage of remaining extract, or imperfectly fermented, with a low percentage of alcohol, and high percentage of remaining extract.

Beers Classified. According to the system of fermentation employed, beers may be classified as follows:

1. Bottom Fermentation.

a. Pilsener
b. Wiener
c. Muenchener
d. Dortmunder
} German lager beers.

e. American lager beers
f. American steam beers

2. Top Fermentation.

g. Mild ales and stock ales	English beers.
h. Porter	
i. Stout	
j. Cream ales	American beers.
Sparkling ales	
Stock ales	
Porter and Stout	
Common beer	
k. Weiss beer	

3. Spontaneous Fermentation.

l. Lambic	Belgian beers.
m. Faro.	

The influence of the system of fermentation on the composition of the beer becomes noticeable, especially in the different quantities of lactic acid produced during fermentation and storage.

Bottom fermentation beers have, as a rule, less lactic acid and fewer bacteria than top fermentation beers; these, in turn, have less than spontaneous fermentation beers.

Bottom fermentation proceeds generally at a relatively low temperature, viz., 43–52° F., but also as high as 45–57° F.

The designation of the two types of fermentation is derived from the fact that in bottom fermentation the yeast for the most part settles on the bottom, whereas, in top fermentation, it rises to the surface.

Bottom fermentation takes 8–16 days; top fermentation about 4–5 days.

In spontaneous fermentation no yeast is added to the wort, the fermentation proceeding slowly through ferments reaching the wort or beer accidentally.

Preservative Principles. The characteristic differences between the English and German brewers' products (ales and stouts—lager beers) consist mainly in the high percentage of alcohol in the former, together with a larger amount of hops employed, the alcohol content of ales and stouts running from about $4\frac{1}{2}$ to 6 per cent by weight, that of lager beer from about $3\frac{1}{4}$ to 4 per cent, that of weiss beer from about $2\frac{1}{2}$ to 3 per cent. The amount of hops employed for ales and stouts averages over 2 lbs., for lager beers from $\frac{1}{2}$ to 1 lb., for weiss beer less than $\frac{1}{2}$ lb. per barrel. The larger amount of alcohol for the English breweries' product, as well as the larger amount of hops employed, are required as preservative principles, the alcohol and hop resins having well-known antiseptic properties, while the German breweries employ refrigeration or low temperatures to preserve the beers in storage from spoiling by checking the

growth of foreign ferments. Weiss beer, which has a relatively low alcohol content and is produced with relatively small amounts of hops and without the application of refrigeration, shows the influences of these preservative principles, inasmuch as this product is made to contain a large amount of lactic acid, produced by the lactic acid ferment, which is left unchecked, as it were, during the production of weiss beer.

The difference in the process of production of English beers and lager beers consists chiefly in the lesser quantity of materials, both malt and hops, employed in the latter, in the low initial mashing temperatures, in lower fermentation temperatures, and very low storage temperatures (about 32 to 34° F.) and in the treatment of the beer after fermentation.

Ales and *stouts* undergo a brisk secondary fermentation on storage. *Lager beer* reaches the storage or stock cellar either thoroughly fermented and then undergoes no secondary fermentation, or it undergoes a slow secondary fermentation, in which case the beers are not chilled on storage to the same extent.

Ales and stouts that are stored for a long period are called "stock" beers. Those which are stored for only a short period, undergoing no secondary fermentation, are called "mild beers." These are usually brewed with less extract (about 14 per cent) and less hops than stock beers, and consequently will not keep in storage for a prolonged period like stock ales.

The difference in the production of *ale* and *stout* consists mainly in the characteristics of the malt and in the treatment of the product after fermentation, ale being produced from pale, or low kiln-dried malt, stout from a mixture of pale malt, caramel malt, and black malt.

Stock ale receives, after fermentation, an addition of hops in the storage cask, whereas stout receives no such addition, with the result that ale undergoes a more brisk secondary fermentation and consequently generally has a higher percentage of alcohol than stout of the same original gravity of wort, while stout contains on this account more extractive substances, and is therefore sweeter to the taste than ale.

Lager beers and *mild English beers* contain considerably less acidity than the English stock beers, which are a little tart to the taste, on account of some acidity taken up mainly during the storage period, from ferments other than culture yeast.

The amounts of lactic acid in the different beers, and which may be considered characteristic of the beers, are as follows:

Weiss beer, about	.50 per cent
Stock ales and stouts, about	.20 to .30 per cent
Mild ales, about	.15 to .18 per cent
German lager beers, about	.10 to .15 per cent
American lager beers, about	.05 to .10 per cent

The acidity in *lager beer* is not due to the development of lactic acid bacteria during its production, but to the development of this organism

during the growth of the malt. Unmalted cereals, which are generally employed in the production of American lager beers, contain no acidity, hence the low quantity of acid in these beers.

Brewing Operations and Equipment, Especially for the Production of Lager Beer. Beer is produced from the materials, mainly barley-malt, hops, water, and yeast, through the processes of cleaning and crushing the malt, mashing of the malt (with or without other cereals); straining or filtering the resulting solution, which contains the extractive substances of the materials, from the grains or insoluble portion; washing out the grains with hot water; boiling this solution, which is now termed wort, before and after adding hops; straining or filtering the hopped wort from the spent hops; cooling of the wort; adding yeast to incite fermentation; drawing off the fermented beer; clarifying and giving life to the beer; racking the beer into trade packages.

Besides these operations, which more particularly concern the character of the finished product, there are many supplementary operations necessary as precautionary measures to insure freedom of the beverage from taint or contamination of any kind, such as foreign odors or ferments, by *varnishing* of all large wooden receptacles, such as tanks and casks; *staining* or otherwise coating iron vessels, such as hop-jack; *pitching* the wooden trade packages, such as barrels and kegs; thorough cleansing of all beer receptacles and utensils, aseptic or antiseptic treatment of all wort or beer conduits and of cellar floors, walls, and ceilings by applying suitable washes, paints or calcimine; treatment of brewing and boiler-feed water, etc.

Brewing Equipment. The modern brewery is equipped with power and refrigerating plant, while the brewing operations proper are carried out in three departments, each so arranged and equipped as to allow of a separate gravity plan of transfer of materials in each, viz., (1) cleaning and crushing of malt in elevator or mill house; (2) brewing operations in brew house; (3) cellar treatment in fermenting cellars, stock cellars, and chip cask cellars. Besides these there are provided a wash house, the pitch yard, and in many breweries the bottling department, or the bottlery.

Mill House. This contains elevators and conveyors for bringing the malt to the *malt storage bins* made either of wood, steel, or concrete, capacity up to about 10,000 bushels; *malt* and *cereal scale hoppers* of steel, round or square, provided with conical bottom; wire cloth cleaning reel; *dust collector; automatic weighing scales; malt mill* to crush malt for extraction, provided with magnets for removing particles of iron.

Brew House, Fig. 346. *Hot* and *cold water tanks; water meter* and gauge. *Cereal cookers* of cylindrical form of steel with stirrer, usually heated with live steam; *mash tun,* a cylindrical vessel of sheet-iron or steel, supplied with a removable perforated strainer or false bottom; also stirring device for mixing malt and water, a steam heating device and

sparger to supply a spray of water to wash out grains, a battery of wort pipes connecting the bottom of mash tun with a copper receptacle called the *grant*; *mash-tun thermometers; safety mash-tun gauge* to regulate flow of wort; *grains tank* of steel with conical bottom, usually outside

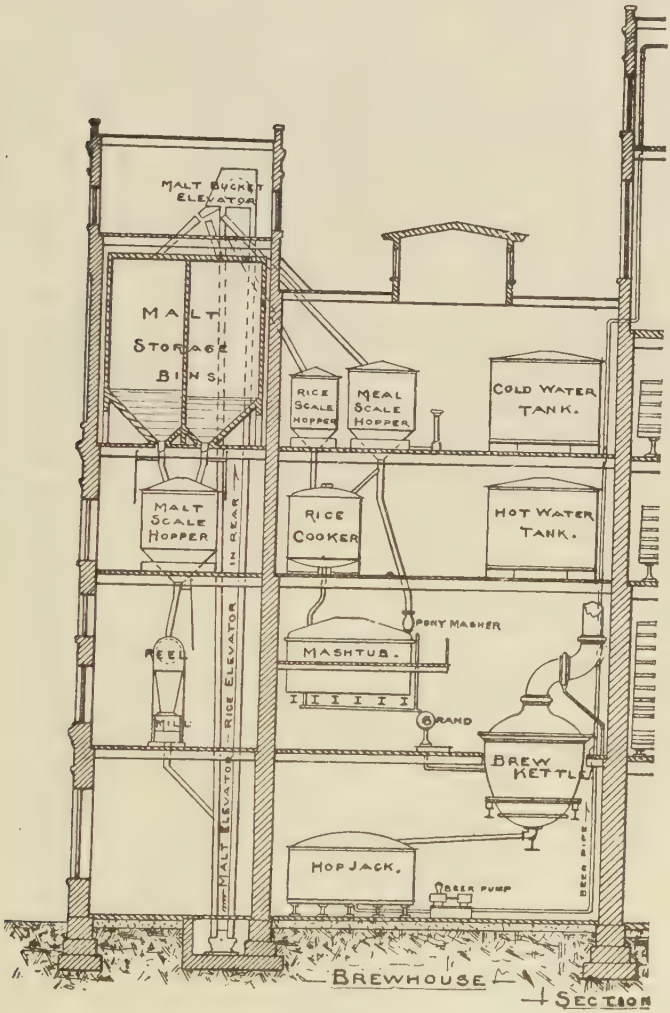

FIG. 346.

of brew house; *grains dryer, mash-tun pumps. Brew kettle* or *copper* in which the wort is collected from the mash tun and is boiled before and after hopping; usually pear-shaped, provided with a steam-jacketed bottom. *Hop-tearing machine* and *screening machine* to separate the valuable ingredients like lupulin; *hop-jack* provided with perforated false bottom to strain out the spent hops; *wort pumps*, piston or centrif-

ugal; *surface cooler*, a shallow iron or steel pan, allowing aeration and evaporation, causing cooling. *Wort* or *beer tank* takes place of surface cooler; *pipe cooler*, the most common being the Baudelot cooler, consisting of a series of pipes arranged in vertical tiers, over the outside of which the wort is allowed to flow; *enclosed* or *double pipe cooler* takes the place of the Baudelot, consisting of a series of tubes forming annular sleeves.

Fermenting Cellar. *Starting* or *settling tubs* of wood used as receptacles in which to start fermentation by adding yeast and in which the sludge or albumen, coagulated in the kettle by boiling, is separated, usually of a size to hold an entire brew. *Fermenting tubs* used as receptacles for the beer during principal fermentation; generally of cedar, holding 50 to 100 barrels and more. *Attemperators*, usually circular pipes or coils with circulating brine; suspended and immersed about 2 feet below the surface of the beer.

Stock Cellar. *Stock* or *storage vats* or tanks are used for holding beer during after-fermentation or ripening process or for general storage purpose, usually of cedar, upright, closed at the top, capacity from 50 to over 1000 barrels; cylindrical glass enameled steel vessels are also used. *Vat supports* consisting of rails supported by cast-iron legs. *Manhole doors*, either outside, closed by lugs, or opening inward, placed near bottom of vats.

Chip Cellar. *Chip casks* in which clarifying and carbonating take place, generally built of quarter-sawed oak, usually barrel-shaped, the large dimensioned ones reinforced by iron rods; also steel construction. *Attemperators* for chip casks are often used, especially in the production of chill-proof bottle beer. *Cask manhole doors; cask supports.* *Bunging apparatus* for maintaining a certain pressure on the surface of the beer in the chip cask and releasing an over-pressure. *Beer filters* are used for the purpose of straining out of the beer any floating particles, such as yeast or albumen. Wood pulp or cotton serves as the filtering material, which is compressed into cakes or cells placed in a suitable copper or steel shell. *Pressure-regulating pumps*, which allow any desired pressure to be put on the beer passing through the filter on its way from chip cask to racking bench, thus reducing necessary pressure on beer in chip cask, and strain caused thereby. *Back-pressure racking machine*, introduced to prevent loss of gas and do away with beer overflow, entailed by old open-style or racking-gut system. The beer enters through a tube inserted through the bunghole of the package, fitting air-tight, and permitting the filling of package against counter pressure. *Carbonaters*, used for the purpose of charging stock beer with carbonic acid gas, usually while the beer is passing from the chip cask to filter.

Wash House. Where returned empty packages are washed. *Automatic barrel washers* soak, convey, scrub, and rinse the packages with little labor. *Barrel elevators* to raise filled packages from one floor to

another or to the loading platform. *Chip washer*, a perforated revolving device for washing chips. *Filter-mass washer*, a vessel in which the filter mass is washed by agitation and flowing water. *Hoop-driving machine*, *pitching machine* and *appliances*, to apply a coat of pitch to

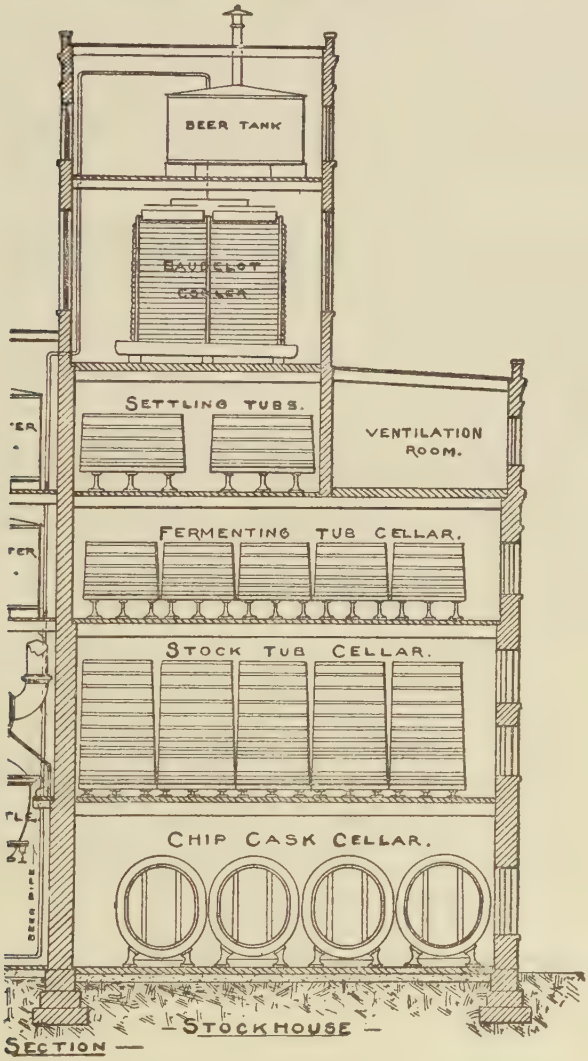

FIG. 347.

the interior surface of the barrels or wooden trade packages, to prevent penetration of wood by beer and consequent souring or infection. Different systems are employed. The old pitch is usually removed by superheated steam or hot air and fresh pitch is introduced either in measured quantity, or by means of a spray, the surplus returning to the pitch kettle.

Bottling Plant. The increasing demand for bottle beer in all parts of the United States has resulted during the last ten years in the establishment of a large number of new bottleries, palatial as to magnitude of establishment and expense of equipment typical of the technical advancement made during that period.

General Arrangement. This must be done with an eye to economy and thoroughness. There should be absolutely no useless or double handling of any bottle or case, and benches or machines should be so placed in relation to each other that they form an unbroken line from the dirty returned bottle to the capped and labeled bottle in the case for delivery.

The bottles are first soaked with caustic soda or other similar solution in a soaking device (tank or machine), from which they are run through the washing and rinsing machine. They are then filled on a filling machine and closed, generally with crowns, but also with corks or other closures, after which they are inspected, sterilized, generally by passing through a pasteurizing machine, and finally labeled, or otherwise finished, and packed in cases or barrels.

In large establishments the filling from barrels carted to the bottlery across the public highway—as required by law—has been generally replaced by filling from government tanks, connected by pipe line from the chip casks directly. Here the casks or tanks, placed in a separate refrigerated room under the bottle shop, are filled and gauged under control of a government inspector.

Equipment. Bottle-soaking tanks usually divided into compartments through which the bottles, by means of endless chains, are carried, filling and emptying automatically with solutions of soda, and finally water. *Washing* and *rinsing machines* for thoroughly cleansing the bottle inside and outside. *Bottle fillers, bottle-closing machines* for cork, patent stopper, crown, or seal. *Pasteurizing tanks* or *machines*, with automatic temperature regulators, containing hot-water baths in which the bottles are immersed or through which they are carried by endless chains in order to be sterilized, the temperature of the pasteurizing bath being maintained at approximately 140° F. *Labeling, dating, wiring machines.* Accessories: tin-foil removers; cork extractors; steaming caps; steaming trays or boxes.

Power Plant. The consumption of fuel in the power plants of breweries is an important economic question and is receiving more expert attention of late. Breweries are therefore found that engage the best technical engineering talent and install the most efficient and up-to-date appliances for the production, transmission and application of power for heating, lighting, cooling, and ventilating.

The *boiler plant*, with its automatic stoker system; the *machine room*, with its steam engines, refrigerating machines, air compressors, dynamos, or motor generators for furnishing power and electric current

for pumps, conveyors, stirrers, for arc and incandescent lamps; ventilators, etc.

Refrigerating Plant. In the production of lager beers low cellar temperatures are necessary. These were formerly obtained by employing ice for cooling the rooms, but a refrigerating plant is now part of every well-equipped brewery. This plant includes the *refrigerating machine;* the piping with *condensers* and *pan;* Baudelot cooler; enclosed coolers, attemperators in fermenting vats and chip casks. The rooms to be cooled are the settling tank room, fermenting room, stock cellar, chip cask cellar, racking room, hop storage room, ice storage.

Refrigerating machines used in breweries are of the compression order, the process being practically the same for all types, the principle being based on the ability of certain gases, usually ammonia, but also carbonic acid and others, to become liquid by compression and cooling, usually by water which absorbs and carries away the heat (in the condenser); and the ability of these gases to evaporate at temperatures required in the cooling pipes or coils, thereby abstracting heat from the surrounding air or liquid, thus lowering their temperature.

Brewing Materials. The materials commonly employed wherever beer is produced are *hops, malt,* and *water.* In some countries, like England, sugars and other adjuncts are used in part with malt; in the United States corn is commonly employed besides rice and sugars. In Germany the employment of any substitutes for or adjuncts to malt is prohibited. Barley is the distinctive cereal that furnishes malt, the exception being wheat used for weiss-beer malt.

Malt and Cereals. Malt is produced from barley by the processes of cleaning, steeping in water, germinating on the floor or in compartments or drums, kiln drying.

Properties of Malt. The berries should be of uniform size and shape; husk and endosperm of light color for pale beers; it should be free from other grain like wheat or oats, or seeds like mustard, rape; odor aromatic, not musty; growth uniform with about 90 per cent of acrospire three-quarters up; condition of endosperm mellow, not flinty; laboratory yield on dry basis about 72 to 74; moisture content not over 6 per cent, lest slackness ensue; strong diastatic and peptic power for proper inversion of starch and albumen; bushel weight not less than 34 nor more than 38 lbs.

Corn is employed, with germ and husk more or less removed, in the form of grits or meal in a separate cooker or in the form of flakes in the mash-tun; *rice,* either broken or as meal, in the cooker; *wheat* in flaked condition in the mash-tun or crushed (by means of malt mill) in cooker.

Malt yields about 64 to 70 per cent of extract in the brewery, of which 4 to 5 per cent are albuminoids; rice about 75 to 80 per cent, corn about 75 to 78 per cent; wheat about 65 to 70 per cent, of which 2 to 3 is albumen; rice and corn yield practically no albumen.

The employment of unmalted cereals like rice and corn offers a number of advantages. They can generally be obtained at a lower price and yield more extract than malt. They lend themselves better to the production of beers of Bohemian or Vienna types than all malt, because American malt generally yields more albumen to wort and beer than European malts, due to higher albumen content of American barley of Manchuria type. American all-malt beers are therefore apt to be more satiating than Bohemian beers with their lower albumen content. The resultant beers are of paler color, of greater stability when pasteurized, and their brilliancy less affected by low temperatures.

The employment of wheat may not be more economical, nor are the wheat beers more stable or less sensitive to low temperatures than all-malt beers. They have a peculiar palatefulness that recommends them in some localities.

Commercial glucose and other brewing sugars are prepared from the starch of corn through inversion by acids at high heats (under pressure). They contain dextrose and dextrin in varying quantities.

Other Adjuncts. Dark malts. For preparing a beer of dark color a malt may be used which has been subjected to special treatment in the kiln, so as to acquire a dark color, such as *caramel malt*, the husk of which is yellowish brown, while the endosperm has a decidedly brown color. In its preparation, ordinary malt of good quality is steeped for a while, so as to take up a certain amount of moisture. It is then dried, and heated in suitable vessels, first to a comparatively low temperature, in order to promote the formation of sugar, and later to higher temperatures at which the sugar is caramelized. *Black malt* is dried at higher temperatures, so that both the husk and the endosperm possess a blackish-brown color. It does not have the pleasant caramel taste of caramel malt. The coloring power is very great. *Malt color* is an extract of black malt, filtered and evaporated to a syrupy consistency. *Roasted corn* is prepared from corn in the same manner as black malt from barley, i.e., by heating to higher temperatures. Its coloring power equals that of black malt.

Hops. Hops as they are used in the brewery are cone-shaped formations, representing clusters of blossoms of the female hop plant. From forty to sixty flowers are grouped together on a central spindle which is zig-zag shaped, forming a so-called hop cone or the umbel of the hop.

At the time of maturity, the seed of the hops and the whole lower and inner parts of the bracts are covered with a fine light-yellow dust consisting of minute granules of lupulin, which contain both the bitter and aromatic principles of the hops, viz., the hop oils and resins, besides hop tannin, hop bitter acids, hop wax, nitrogenous bodies, carbohydrates and mineral substances, an enzyme (diastase) which is of special importance in ale brewing.

Up to 1808 hop culture remained confined to three New England States, Massachusetts, Vermont and Maine. Later the hops from New

York State were found not only superior in quality, but three times as prolific. About 1860, small patches were planted to hops in Wisconsin and Michigan but by 1880 hop cultivation was well introduced in California, Oregon, and Washington, which States, together with New York, now furnish the hops for the American market, while large quantities are also exported.

Water. A good *brewing water* should be clear, bacteriologically pure (uncontaminated by sewage), free from odor or taste; moderately hard, with a moderate amount of sulphate of lime, and common salt, free from iron and alkali. Such water is also adapted for malting; for washing of tanks, bottles and barrels, filter mass; for watering yeast, and dissolving isinglass. For the *steam boiler* the softest water is the best if free from odor; for *cooling* it should be free from acids and not too hard.

FIG. 348.—Hop Cone (Unripe Stage).

FIG. 349.—Hop Cone (Ripe Stage).

If water does not come up to requirements it may be improved by filtration, by boiling, by hardening, by supplying deficient mineral matter (Burtonizing) especially practiced in ale brewing; by softening and by purification.

Varnish. Wooden vessels in the brewery, like starting vats, fermenting vats, stock tubs, and chip casks, are varnished for the purpose of preventing any extractive matters that may remain in the wood from getting into the beer. At the same time the varnish prevents the beer from penetrating into the pores of the wood where it would sour and become a source of infection that would subsequently attack the beer run into the vessel. The most common varnish is a solution of shellac in special denatured grain alcohol; raw wood-alcohol is extremely poisonous.

Pitch. Trade packages are internally covered with a coat of pitch for similar purposes to those which lead to varnishing storage casks, etc., i.e., to prevent the beer from coming into contact with the wood. Ordinary brewers' pitch, most commonly used, is the purified resin of certain conif-

erous trees, as pines, firs, called turpentine. The resulting colophony is softened or made pliable by melting with some rosin oil, cotton-seed oil or paraffin.

Clarifying Chips are used at the expiration of the storage period; these being strips of wood, usually beech or maple, 6 to 12 ins. in length, with a thickness one-twelfth of an inch. They should be well seasoned and carefully boiled out.

Isinglass for beer clarification is derived from fish sounds, or hide of the calf, containing gelatine as active principle.

Brewing Operations. Brewing operations proper include all operations conducted in the mill and brew house, viz., cleaning and crushing the malts; mashing; straining; boiling before and after hopping; hop straining; cooling.

Mashing Systems. Different methods of applying temperatures to a mash supply the following systems:

1. Infusion or water mash: English beers. High initial temperatures.
2. Decoction or thick mash: German lager beers. Low initial temperatures.
3. Malt infusion and unmalted cereal decoction mash: American lager beers. Low initial temperatures.

By the infusion method the mash is brought to its final temperature by the admixture of water of suitably high temperature. By the decoction method, part of the mash itself is raised to a boil and then returned to the mash tun. The unmalted grain is boiled separately with some malt and run into the malt mash to produce the final temperature.

American Brewing Operations. Cleaning and crushing the malt in a *roller mill;* mixing the grist with water, approximately 100 lbs. of malt per barrel, at 100° F., in the *mash-tun,* which contains false bottom and stirrer; holding the mash here for peptic action for about one hour; when boiling hot rice or corn mash or hot water is run in, raising temperature to about 154° F., maintaining this temperature for about 15 minutes for diastatic action, and raising to final temperature of about 165° F. in 15 minutes, resting the mash about 30 to 45 minutes; tapping; straining, when clear, into kettle; sparging the grains left in mash-tun with water of 165° F. until thoroughly extracted; boiling wort in *kettle* before addition of hops for about one hour, and one hour more with hops; running brew into *hop-jack,* straining out the hops; pumping wort to wort tank, running over Baudelot cooler into fermentation starting vat, where it is yeasted. *Rice* or *corn* are generally mashed in a separate cooker together with a part of the malt, and when boiled sufficiently long the mash is united with the malt mash in the mash-tun.

American Lager Beer. *Pale Lager Beer.* Strength of wort, 12 to 13 per cent extract. Material, 50 to 55 lbs. per barrel, of which about

two-thirds should be pale malt and one-third may be unmalted cereals, like corn grits, corn meal, corn flakes, corn starch or rice. Sugars like glucose may also be employed to the amount of about 25 per cent in place of unmalted cereals.

Malt Beers are brewed with 12 to 15 per cent extract, and require 50 to 60 lbs. of malt per barrel.

Pale Draught Lager Beers should be brewed with 12 to 13 per cent extract, and require from 45 to 53 pounds of material, of which two-fifths may be unmalted cereals.

Pale Bottled Lager Beers should be brewed with $12\frac{1}{2}$ to $13\frac{1}{2}$ per cent extract, and require from 52 to 60 lbs. of material, three-fifths of which may be malt and two-fifths unmalted cereals.

Temperance Beers are brewed with about 7 to 8 per cent extract.

Malt Tonics are brewed with about 15 to 18 per cent extract.

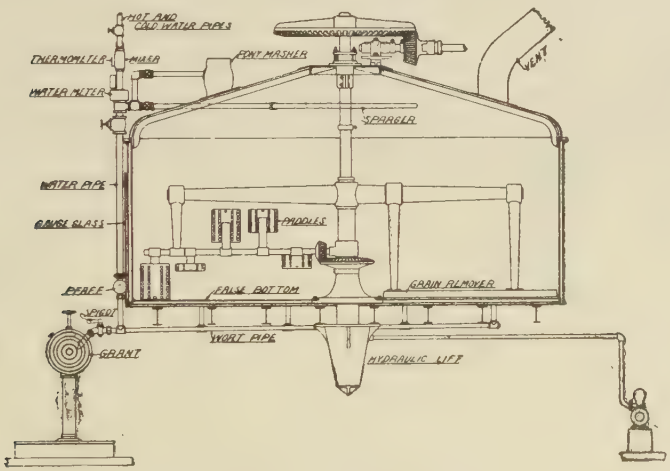

FIG. 350.—Mash-tun and Apparatus.

Principles of Mashing. Mashing is the process of extracting the goods by mixing them with water at suitable temperatures and in proper relative quantities, preparatory to boiling in the kettle.

Chemically it proceeds in the main by the inversion of the starch into maltose, malto-dextrin, and dextrin, and the modification of the insoluble albuminoids into a soluble form. These changes are brought about by the agency of two substances which are contained in the malt, and begin operations when the malt is mixed with water at definite temperatures.

These substances are called diastase and peptase. They were formerly called chemical ferments as distinguished from the organic ferments which are responsible for fermentation. At the present day the term enzymes, or soluble ferments, is more commonly applied to them. It is the function of the diastase to invert the starch, of the peptase to modify the albuminoids of malt, as above indicated.

The amounts, both absolute and relative, of dextrin, maltodextrin and maltose, as well as of the modified albuminoids like albumoses, peptones and amides, finally present in the wort, are materially affected by the conditions under which the enzymes do their work. Hence, it is in the power of the brewer to control the composition of the wort, within certain limits, by modifying such conditions.

It generally being desirable to obtain beers with a high degree of palatefulness and foam stability, properties dependent in the main upon the amount of unfermentable extractive substances left in the beer, among which there should be a sufficient amount of the desirable albuminoids or proteids, the mash is generally peptonized at low temperatures, for instance 100° F., for about one hour, while the starch is inverted at higher temperatures, for instance, for fifteen minutes at 154° F.—slowly raising to 165–166° F.—the latter usually being the final mashing temperature. The peptonizing enzyme "peptase" is most active at about 100–120° F.; diastase at about 140–154°; over 170° the diastase becomes very weak.

Malt contains diastase in quantities sufficient to convert into maltose more starch than that which is stored up in the malt itself, and American malts on an average possess a much greater diastatic strength than German malts; in fact, their power in this respect is so great that there is danger of carrying saccharification too far, if the mashing temperatures that are customary in Germany were retained. Hence, the principles of raw cereal brewing became the subject of closer study in this country.

Water. The amount of water to be employed in the production of 100 barrels of wort or about 100 barrels of beer, is approximately 135 barrels. Some of the water employed is left in the grains (about 20 barrels), some is evaporated in boiling (about 10 barrels), some is evaporated on the Baudelot cooler (about 5 barrels).

With *grits* and *meal* use: For 100 lbs. of material in rice tub, 1 barrel of water; for 100 lbs. of corn, 30 lbs. of malt. Boil grits 75 minutes, meal 45 minutes.

While the mash machine is in operation, a slow stream of water should be forced continually through the underlet (pfaff) to keep openings clear; also directly after stopping machine after reaching mashing-off temperature.

Live Steam can be employed directly for heating the mash, if the water used for boiler feeding is of good or medium purity, i.e., if it does not impart to the steam any obnoxious substances. Care should also be taken in the selection of a proper boiler compound for the same reason. Instead of heating with live steam the mash-tun may be provided with a steam jacket or coil. When the end temperature is reached, a sample of the mash should not show any starch by the iodine test.

Let the all-malt mash rest thirty minutes and the cereal mash forty-five minutes. If allowed to remain standing too long the grains will settle too firmly.

Tapping. Open the taps wide, one by one, for a few seconds, and close them again; the recoil of the liquor will rinse out underdough. Then open the taps gradually until a proper flow of wort is obtained. Pump the wort back into the mash tub as long as it runs turbid, which usually lasts eight to fifteen minutes. The wort should then flow quite bright.

Sparging. This process consists in sprinkling hot water over the grains to wash out as much as possible of the valuable constituents remaining in them. The amount of sparging water should be considered when starting the mash, with reference to the total amount of wort desired.

Boiling the Wort. The wort obtained by mashing is boiled for a certain period for the purpose of eliminating or rendering harmless certain undesirable constituents, like coagulable albuminoids, and introducing other new bodies, like hop resin and hop oil, by extraction from the hops. Besides, during heating and boiling the wort assumes a darker shade, due to caramelization of the sugars; water evaporates, resulting in a denser liquid, and the tannic acid of the hops coagulates an additional quantity of undesirable albumen, this coagulation aiding in clarifying the wort and causing it to "break."

In the United States the wort is generally heated by steam jackets and sometimes by steam coils, direct fire kettles having gone quite out of use. Steam is turned on when the wort flowing from the mash tub covers the heating surface in the copper, and the temperature kept at about 190° F. (70° R.) until all the wort, including spargings, has run in. Unless very pale beer is desired, the brewer may bring the wort to a boil while it is flowing in. During the boiling period the wort should be kept in a state of vigorous ebullition.

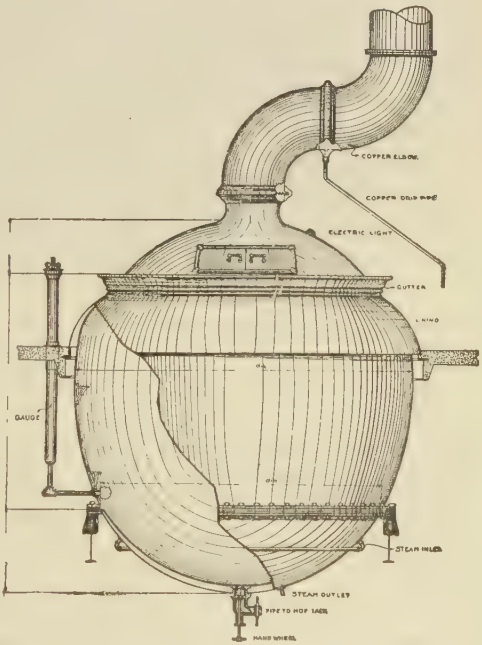

FIG. 351.—Brew-kettle.

Straining. From the copper, the wort runs into the hop-jack, where it is allowed to stand for a period, to permit the hops and albuminoids to settle.

The wort should not be allowed to rest longer than fifteen minutes, as a dark color or rank, bitter taste may result if wort is left in contact with hops too long. The hop-jack is provided with a false bottom, through

which the wort is drained into a pump that delivers it to the coolers. The hops remaining on the false bottom are sparged with hot water to wash out the wort they contain. If the wort remains in hop-jack very long, or if the spent hops are pressed out to obtain the wort, a rank bitter taste of the beer is apt to result.

Cooling. The wort reaches the *surface cooler*, a large, shallow iron pan, and remains here a short period for the purpose of preliminary cooling. The wort should be cooled to 145° F., and not lower, on the surface cooler, and receive proper aeration during cooling, avoiding all sources of contamination in the meantime. Aeration of the wort during cooling has the effect of further precipitating undesirable albuminoids. Besides, the wort absorbs air, which is utilized by the yeast later on. Most of the microbes that reach the wort below 145° F., will remain alive, the most

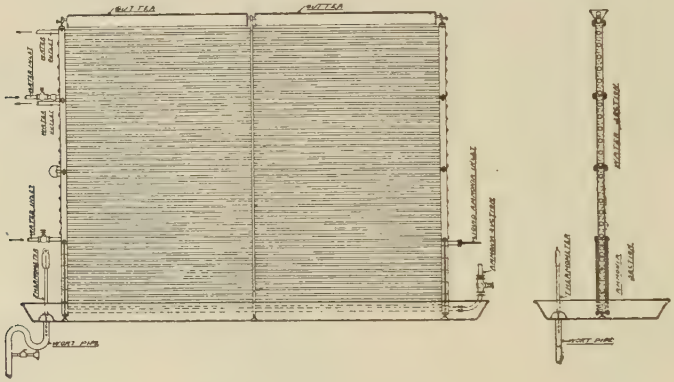

Fig. 352.—Baudelot Cooler.

common ones being butyric and lactic acid ferments and wild yeasts. Instead of a surface cooler, a wort tank is more frequently employed.

Baudelot Cooler. After the preliminary cooling the wort is sent over the Baudelot cooler, where it should be cooled down to 48° F., which is sufficiently low. Formerly it was a general rule, however, to cool the wort to as low a temperature as 42° F. The Baudelot cooler is a pipe cooler, in two sections, the upper one cooled by water, the lower one by brine or ammonia. The wort runs down over the outside surfaces of the pipes.

Enclosed Cooler. These have been taking the place of the former in many breweries of late. The wort circulates through a pipe system and is cooled through a counter current of water until it reaches the brine or ammonia section. Artificial aeration must be provided.

Cold Break. After the wort leaves the coolers it should show a good "cold break," that is, it should settle clear in the sample glass at a temperature below 40° F., or filter clear. If it does not, the turbidity may be due to unconverted starch, to albumen, or to infection.

Loss in Volume. A certain loss in volume will occur on the passage of the wort from kettle to settling tank, due to (1) contraction in cooling, about $4\frac{1}{4}$ per cent; (2) evaporation of water, about 5 per cent; (3) adhesion of liquid to surfaces of vessels, pipes, etc., about $\frac{1}{2}$ per cent. When hops are properly sparged it will take about 107 barrels of wort in the kettle to obtain 100 barrels in the cellar.

Fermenting Cellar Operations. *Pitching with yeast.* Fermentation is induced in the wort by adding yeast properly prepared, which operation is termed "pitching." The common practice is to mix the yeast with an equal quantity of finished wort or boiled *first wort* of about 55–60° F., rouse well to insure aeration and breaking up of cell aggregations, transfer to settling tank when the mass is in fermentation, mixing with it the wort as the latter runs from the cooler.

Amount of Yeast. The amount of yeast needed to secure a normal fermentation is from $\frac{3}{4}$ to $1\frac{1}{2}$ lbs. per barrel; the lesser quantities sufficing with lesser densities of wort, greater yeast vigor, better aeration.

Fermentation Phenomena. Within fifteen to twenty-four hours, according to the pitching temperature, little white bubbles appear around the sides of the vessel. The beer at this time is covered with a dark head of a thick consistency, composed largely of albuminoid matter, coagulated during the boiling period (sludge). The head of impurities being skimmed off, the whole surface is found to become quickly covered with a fine white froth (" whitening over "), rather higher around the rim than in the middle, denoting that carbonic acid gas is escaping through the fermentation of the sugar (maltose).

Kraeusen. The head of froth begins to move from the sides of the vessel to the middle, and assume a frizzled appearance, small cockle-shaped mounds beginning to rise all over the surface. At the expiration of twenty to thirty-six hours after pitching, the surface should be curly and pure white (" young kraeusen "). From the time the froth head begins to move toward the middle, fermentation becomes more active, the head rising all the time (" high kraeusen "). At the same time the temperature rises, slowly at first, more rapidly as the activity of fermentation increases, while the saccharometer indication or density decreases more rapidly, the drop amounting to one-fourth to one-half of one per cent a day in the early part, and reaching one to one and one-half toward the high kraeusen stage. The curly head of froth turns a darker color while rising in height.

The high kraeusen stage is reached seventy to eighty hours after pitching and is maintained for a period of forty-eight to seventy-two hours, varying according to different influences. During this time the fermenting beer is kept at a certain low temperature, 48 to 50° F., and as high as 58° F., by means of attemperators, and when the head begins to collapse is cooled slowly to 39° F. The saccharometer falls more slowly as the end of the principal fermentation draws near. When the end is

reached, the fall of the saccharometer is commonly $\frac{1}{10}$ to $\frac{1}{30}$ per cent in twenty-four hours.

The yeast, which had been kept in suspension during fermentation through the escape of carbonic acid gas, should now be found settled on the bottom of the fermenter; the amount being about three to four times the quantity used for pitching.

Sample Glass. In a sample glass the beer should show quick sedimentation and clarification in about twenty-four hours at cellar temperature.

Yeast Properties. Yeast has a thick, stiff pasty consistency, not watery or slimy, a yellow to brownish color, a bitter taste due to hop-resin, and a characteristic odor.

It consists, for the most part, of single cell organisms of the class saccharomyces and species cerevisiæ. Yeast mechanically encloses a large amount of water or beer—about 50 per cent—through which are dispersed minute bubbles of carbonic acid gas, that escape when the yeast is stirred, emitting a rustling sound. After the beer has run from the fermenter, the yeast sediment should be quite firm and thick. However, unless an absolutely pure culture, every yeast has an admixture of foreign organisms, as bacteria, wild yeasts, and mycoderma. All these impurities may be classified as "potentially dangerous."

Yeast Type. The course of the fermentation as performed by the yeast depends not only on the vitality and environment of the yeast, as age of yeast, temperature, aeration, composition of nutritive medium, presence or absence of other organisms, but also upon the type of yeast employed, which may be distinguished by differences in properties possessed, or effects produced by them.

Types of cultivated yeast are distinguished by differences in the following properties possessed, or effects produced, by them:

1. Degree of attenuation;
2. Fermentative energy, or rapidity of attenuation;
3. Reproductive energy, or growth of yeast;
4. Rapidity of settling of yeast, or clarification of beer;
5. Compactness of settling of yeast;
6. Qualities of beer obtained, as taste, odor, and durability.

Yeast Clusters. The grouping together in clusters of micro-organisms like yeast, is brought about by a mucilaginous secretion of the cell membrane, so that cells which come in contact stick together in larger or smaller cell aggregations or clusters or flakes. This gives rise to a more rapid settling of the yeast, that is clarification, after principal fermentation on storage and in chip cask, and more compact settling of the yeast in fermenting vat and yeast vat, a better break of the beer, and is of influence regarding attenuation. Low attenuating types form larger clusters than high attenuating types, while wild or foreign yeasts do not have the faculty to any extent.

Stock Cellar Operations. *Tanking the Beer.* The beer is brought from the fermenting vat to the stock tank either at the temperature to which it has been cooled in the fermenter and then it undergoes a secondary fermentation, or it is further chilled on its way to the stock cellar, passing it through a cooler in which case no secondary fermentation is anticipated and the beer should reach the stock tank thoroughly fermented.

Storage is that stage in which the beer is kept after the conclusion of the primary fermentation and prior to final clarification for the trade package.

The objects of resting the beer are to eliminate certain suspended matter, like yeast, thereby securing greater clearness, and certain objectionable matters, like albumins, thereby securing greater durability, especially in pasteurized bottled goods.

During the storage period there should be a slight progress of secondary or after-fermentation, unless final attenuation was reached previously. The residue of maltose and part of the maltodextrin are fermented by slow degrees, the amounts of carbonic acid and alcohol increasing.

The yeast settles the more quickly, the less sugar there is present and the smaller the storage vats; the albumins are the more thoroughly eliminated, the better the mash was peptonized, the lower the storage temperature, and the longer the period of storage. Hence, long storage at low temperatures enhances the stability of beer after pasteurization.

Starch particles do not settle on storage. Nor can dependence be placed on improving the beer through long storage in respect to number of bacteria it contains. On the contrary, bacteria may increase during storage.

Low temperatures while the beer is in storage are necessary to precipitate the albumins and to check the development of bacteria. The storage cellar should be kept as near to the freezing point as possible.

Chip Cellar Operations. When sufficiently matured in storage, the beer is run or pumped into chip casks, so called from a method of clarifying beer by means of chips .

Treatment in the chip cellar has a two-fold object:

1. To impart to the beer the necessary life, that is, a sufficient amount of carbonic acid gas so that it will foam properly when tapped. This is done:
   - *a.* by kraeusening and bunging, or
   - *b.* by charging with carbonic acid gas directly (carbonating), or
   - *c.* by both kraeusening and carbonating.
2. To make the beer brilliant. This is done:
   - *a.* by the addition of chips;
   - *b.* by the addition of isinglass;
   - *c.* by filtration.

Kraeusening. This consists in the addition of kraeusen beer, that is, young beer in the first, or kraeusen stage of fermentation, twenty-four

to forty-four hours after pitching, the amount being about 15 per cent for home draught beer; 10 per cent for export draught or bottle beer, or 5 per cent when beer is carbonated. A few days after the kraeusen have been added the finings are introduced and the cask is bunged, to prevent the escape of the gas generated by the kraeusen, its accumulation causing a pressure which is termed *bunging pressure* and which is allowed to rise to about 5 lbs.

Carbonating. Carbonic acid fermentation gas may be introduced into the beer at any stage after fermentation, but usually this is done while the beer is being transferred from the chip cask to the racking bench and before it reaches the filter. When beers are carbonated they are either not kraeusened at all or only with relatively small quantities of kraeusen; about 5 or 6 per cent. The gas is introduced either on the *pressure* principle by spraying the beer through a compressed atmosphere of gas or on the *aspirator* or *injector* principle, by forcing the gas into the beer, usually in a conduit while in motion.

Clarification. Matter remaining in suspension at the end of the storage period is eliminated by mechanical means. First among them is the introduction of chips. *Beer chips* or *clarifying chips* are strips of wood, usually of beech or maple, so cut as to present a maximum of surface with a minimum of volume and weight. The chips are spread in the bottom of the chip cask, where they retain particles in suspension, reaching them as well as the sedimentation caused by the employment of isinglass. Chips must be carefully prepared by boiling in water, with an addition of soda.

Fining the Beer. Brewers' finings are prepared from so-called *isinglass*, obtained either from *fish* through cleaning, rolling and drying the bladder, or from *hide* of *calf*. The finings may be prepared on the cold or warm plan, their efficiency depending upon the amount of gelatinous substance the isinglass yields and which in flocculent form distributes through the beer enveloping the suspended particles and carrying them to the bottom. One pound of isinglass is sufficient for one hundred to five hundred barrels of beer.

Filtration. The process of filtering beer consists in forcing the beer on its way from the chip-cask to racking apparatus, generally by means of air pressure applied at the chip cask, or through a pressure regulator pump interpolated between chip cask and filter, through one or more layers of compressed fibrous material, called filter mass, which commonly consists of cotton fiber. Beer should always pass through the filter under back pressure, as it will otherwise foam to such an extent as to preclude the proper filling of the trade-packages. It should stand in a cold place, if practicable, in the chip cellar.

Back-pressure Racking. The principle of back-pressure racking is to create in the delivery package a back pressure sufficiently high to prevent foaming of the beer, so as to permit of readily filling the package

without loss of time and without the foaming and loss of beer accompanying the practice of "gut racking" which formerly obtained.

Special Brewing Systems. The practice of storing the beer for a long period in cold cellars is a rule with some exceptions. Different systems have been installed to obviate this necessity, the principle being to obtain complete or final attenuation in the fermenting vats. Such systems are:

Pfaudler System. Employing glass enameled steel tanks throughout and vacuum and aeration for completing fermentation; finishing the beer by kraeusening; *Schneible system,* with high fermentation temperatures; chilling and carbonating beer from fermenter to finishing tank; *Selg system,* giving attention mainly to yeast culture, the constructive copper or steel fermenting vat with conical bottom permitting removal of sedimentation at any time; *Nathan system,* only tried experimentally in Europe, aiming at cooling of hopped wort, aeration, fermentation, chilling, carbonating and finishing—all in one tank.[1]

Prohibition Near-beers. At this writing, 1918, in 25 States of the Union legislation has been enacted prohibiting the manufacture and sale of alcoholic or intoxicating beverages.

In about half of these prohibition includes all beverages containing in excess of 0.5 per cent of alcohol, in a considerable number of States beverages under 0.5 per cent of alcohol are prohibited if they are prepared from malt, being classed as malt liquors whether they contain alcohol or not. In practice beverages containing no more than 0.1 per cent of alcohol are considered alcohol free, while State chemists are not agreed whether they can lay claim to the identification of malt beverages by analysis. In fact malt-near-beers and alcohol-free beverages resembling beer in many respects have been placed on the market prepared from bran as a diastatic basis in place of malt.

Washington Prohibition Law. As an example of a State prohibition enactment including malt liquor, we quote the following from the Washington law:

"*An Act* relating to intoxicating liquors, prohibiting the manufacture, keeping sale and disposition thereof, etc.

"The phrase 'intoxicating liquor,' whenever used in this act, shall be held and construed to include whisky, brandy, gin, rum, wine, ale, beer and any spirituous, vinous, fermented or malt liquor, and every other liquor or liquid containing intoxicating properties, which is capable of being used as a beverage whether medicated or not, and all liquids, whether proprietary, patented or not, which contain any alcohol, which are capable of being used as a beverage."

Near-beers with less than 0.5 per cent of alcohol may be produced from regular brews by de-alcoholizing the fermented product through boiling

[1] For American Pasteurized Bottle Beer, see Bottling Plant, succeeding Brewing Equipment.

out or evaporation in vacuo; and carbonating or kraeusening the product. De-alcoholization may extend down to less than 0.1 per cent. Another method is to prepare a brew with about one-half the usual gravity; add yeast and after about twenty-four hours chill so as to check fermentation. When alcohol content has reached about 0.2 to 0.3 per cent, then filter, carbonate, bottle and pasteurize.

In Other Countries. In Canada under prohibition enactments beverages may contain up to $2\frac{1}{2}$ per cent proof spirits or about 1.2 per cent of alcohol by volume. In England the permissible percentage is approximately the same. In Denmark beverages up to $2\frac{1}{4}$ per cent by weight or approximately 3 per cent by volume are tax free and considered non-intoxicating, and in other Scandinavian countries like Norway and Sweden, similar exemptions are made.

English Top Fermentation Beers. The beers brewed in the United Kingdom and its possessions show similar characteristic differences in their properties as the German beers. They are called *ale, porter* and *stout.*

Mild beers, whether ale, porter or stout, are such as undergo no secondary fermentation, but are marketed about seven days after the principal fermentation is finished.

Stock beers, or *old beers,* whether ale or stout, are such as have undergone a secondary fermentation and are stored about two months or more before marketing.

The mild beers are distinguished from the stock beers by a more sweetish (mild) taste, containing more unfermented malto-dextrin and less acid, the old beers, on the other hand, becoming more alcoholic and tart. There is, therefore, much difference in the properties of mild beers and old or stock beers.

Mild ales are usually brewed of a darker color than old ales, with less original gravity and less hops.

Old or *stock ales* have a pale to amber color, quite bitter and more or less tart taste, strong hop flavor, and though brewed with a high percentage of extract, have less extract left, but contain more alcohol than stout, which is mainly due to the practice of dry-hopping ales, which results in breaking down the malto-dextrins more effectually than is the case with stout, which is not dry hopped.

Stouts are quite dark, almost black, have a pronounced malt-caramel taste and aroma, a sweetish taste if mild, and a more or less tart taste, according to age and circumstances. They are brewed stronger than ales.

Porter is brewed less strong than the old beers. It stands in a similar relation to stout as does a mild ale to a stock ale.

Brewing Materials in England. The materials used in England, besides malt, hops and water, are usually sugars of different kinds. Such are caramel (produced from glucose) for black beers, invert sugar and glucose for mild and stock ales, while of late years, rice, maize and wheat are gaining in favor. The English drinking public now prefer beers of

low gravity to the stock beers, and since they should contain only a moderate amount of alcohol, but sufficient extract to be full to the palate, sugars should be used for these beers, containing the requisite amount of unfermentable extract.

Malt. Most brewers use some foreign barley malt, together with that produced from domestic grain, on account of the better clarification of beer and better drainage of wort, while some brewers use California barley malt entirely, the beer from which keeps better in hot weather. Usually pale malt is employed in the production of all the beers, together with some coloring material, preferably caramel, brown malt, amber malt or roasted corn for dark ales, porter and stout. Sometimes black beers and mild ales receive an addition of caramel solution in the fermenting vessel just prior to the close of the principal fermentation. For dark beers higher kiln-dried malts are preferred by many brewers.

Hops. With regard to hops, the English brewer favors the employment of foreign qualities of hops to blend with the domestic article, the proportion frequently rising to 50 per cent, chiefly American hops or "Yankees." The English hops are distinguished for their delicacy of flavor, especially the East Kent goldings, and these are eagerly sought for flavoring choice pale ales in dry hopping. The relative quantities of hops and of other materials to be used in brewing the different beers, according to the gravity of wort and other requirements, may be gathered from the introductory remarks in the paragraph on "Brewing" also salient differences in regard to the brewing process employed for the different types of beers.

Brewing Operations for English Beer. The method of mashing is essentially the same for ales and stouts whether of the "stock" or "mild" type. The crushed malt is passed through a "pony masher," where it strikes and is mixed with the mashing water of about 165° F. for ales, and slightly lower for stouts, the initial or mashing temperature being about 150° F. for the former and 145° F. for the latter. After thorough mixing in the mash-tun the temperature is brought up, by underflow of hot water, to 154°, the stirrer is stopped, and the taps are opened after about two hours. The grains are sparged with water of about 170 to 160°. The wort flowing into the kettle is kept heated to near boiling-point until full, when hops are added (1½ to 3 lbs.) and boiling (simmering) continued from one to two hours, when it is "turned out" into hop-box, strained, pumped on surface cooler, then run over pipe cooler, and yeasted at 58 to 60° F.

Top-fermentation Appliances and Operations. The essential difference between top fermentation and bottom fermentation is in the behavior of the yeast, which rises to the top during top fermentation, where it is either removed by suitable implements, by a process called "skimming," or it is allowed to work out of an aperture at the top of the fermenting

vessel, by a process called " cleansing." If the cleansing takes place in casks, the yeast working out through " swan necks " into a common trough, it is called " Burton union system "; if through openings (lips) in the top and edge of upright tanks, the tanks themselves being so placed as to form a trough for the yeast, it is called " Ponto system." Then there is a combination of the skimming and the cleansing systems in the " stone square system," the yeast working out through the top of a closed stone square, from where it is removed by skimming.

Secondary Fermentation. Most English beers are sent out directly after racking, dry hopping and fining, without going through any secondary fermentation. Stock beers, however, undergo a secondary or slow fermentation in the storage or trade cask. The malto-dextrins of the beer supply the substance for this fermentation, being partly degraded by inversion enzymes contained in the yeasts and by the diastase introduced in dry hopping. Thus, beers that are dry hopped ferment down lower in the cask than beers unhopped in cask, like most black beers. The fermentation of the sugars, formed by the breaking down of the dextrins, keeps the beer charged with carbonic acid gas, and this condition is essential for checking the development of foreign ferments. Therefore, a sound secondary fermentation is of the greatest importance.

Dry Hopping. Ales usually, and black beers sometimes, receive an addition of hops in the storage or trade cask, the quantity varying from $\frac{1}{4}$ lb. for mild ales to 1 lb. per barrel for pale, bitter and stock ales.

Priming. Often a solution of some kind of sugar is added to the beers, especially the black beers, in the cask, which process is called priming. The object is to impart sweetness or body, or to aid secondary fermentation and give " life " or what in England is termed " condition " or " briskness."

Vatting. In many breweries it is still customary to blend a young beer with an old one that shows acidity and proper flavor in a marked degree, in order to give the product the character of age. Especially is this done with stouts. The old beers are called vats, and as much as 25 per cent is blended at times with the young beer.

Bottling Ales. Ale for bottling should be (according to Wright) allowed to go through all its cask changes, spontaneous brilliancy (unaided by finings) at the end of them being the simplest criterion for bottling.

American Ales. In the United States a somewhat different system of brewing has developed in the production of top-fermentation beers, from those employed in England. While the American stock beers are patterned after the English stock ales and stout, *cream*, *lively*, or *present use ale* takes the place of the English mild ales, and more recently the American ale brewers have equipped their plants with refrigerating machines to brew a beer—*brilliant* or *sparkling* ale—that combines the properties of lager beer and ale, i.e., a sparkling, brilliant beer with an ale taste and aroma. Since these ales have been put on the market, top-

fermented beers have gained some of the ground which they had lost in competition with lager beers.

In the main, the equipment of a modern American ale and porter brewery does not differ essentially from that of a lager beer brewery. The chip-cask cellar of the lager beer brewery, however, can be dispensed with, a carbonating room taking its place, while the stock cellar is retained, since some of the ales are stored.

Berliner Weiss Beer. Of the many varieties of top-fermentation German beers, it is only *weiss beer* that has been able to compete with the lager beers, while the others, being gradually displaced, are but little known, or enjoy only a local reputation.

Berliner weiss beer should have a very pale color, be moderately clear, distinctly tart, rich in carbonic acid, so that it foams strongly when poured, and should hold the foam moderately well. The difference in the production of weiss beer and the other beers described consists in the materials employed, which is generally one-third barley malt and two-thirds wheat malt; in the gravity of the wort, which is usually below 10 per cent; in the quantity of hops used, usually less than $\frac{1}{2}$ lb. per barrel; in the fermentation, during which lactic acid bacteria are allowed to develop, the weiss beer yeast containing these in large numbers, and in the treatment after fermentation, the weiss beer not being stored but mixed with fermenting beer, which mixture being filled into bottles—where fermentation continues—results in a large quantity of carbonic acid gas being retained in the bottles, and gives to the finished product the characteristic life. The large amounts of lactic acid bacteria do not permit of clarification of the product, whereas ales and stouts are usually clear and lager beer usually brilliant.

Lager Beers in Germany and Austria. Besides the recognized types, like the *Bohemian, Vienna* and *Bavarian* beers, of each of which there are brewed two varieties, the *Schenk* or *winter beer*, and the *lager* or *summer* beer, there are brewed for special purposes beers of each type like *Bohemian export, Vienna export* or *Bavarian export*, or beers brewed for special occasions, like *bock*.

Bavarian Beer is light brown (like the Munich) to dark brown (like the Kulmbacher). It has palatefulness, a sweetish taste and malt flavor, moderately attenuated through fermentation (65 to 70 per cent) original gravity of wort $12\frac{1}{2}$ to 15; for bock and export 15 to 18.

Bohemian Beer (like the Pilsener) is light yellow to greenish yellow, the taste is vinous, dry, somewhat sharp, bitter taste of hops predominates. More strongly attenuated than Bavarian, 70 to 75 per cent. Schenk beers brewed $10\frac{1}{2}$ to $11\frac{1}{2}$; lager and export $12\frac{1}{2}$ to 13.

Wiener Beer is less bitter and darker in color than Bohemian and has less malt aroma and is paler than Bavarian. In all respects it takes a medium position between both. Schenk beer about 11; export or "Maerzen" about $14\frac{1}{2}$ to 15.

Kulmbacher. A very dark beer with the Bavarian characteristics

especially accentuated, brewed along the lines of a Bavarian lager, from a very strong, original gravity of wort of about 18 to 19 per cent.

Dortmunder. Pale, like Bohemian, of about 14 to 15 per cent; from low dried malt; strongly hopped, highly attenuated.

Export and *Bock* differ from the Schenk and lager in that they are brewed stronger and contain more alcohol. Thus the percentage of alcohol and extract found, as the result of the analyses of a large number of beers, was on the average: [1]

	Alcohol.	Extract.
Schenk or winter beer	3.36	5.34
Lager or summer beer	3.93	5.79
Export beer	4.40	6.38
Bock, Doppel, or Maerzen	4.69	7.21

For general character of these beers refer to introductory remarks in the paragraph on "Brewing," also for materials employed and brewing processes.

The *mashing method* is peculiar, inasmuch as three parts of the whole mash, called the first, second and third mash, are successively boiled each for ten to forty-five minutes, and returned to the mash tun. In Bohemia, where pale beers are the vogue, boiling is often restricted to ten, fifteen or twenty minutes, in Vienna generally thirty minutes, in Bavaria often forty-five minutes. By returning the boiled portions the mash is successively heated from 95° F., the initial temperature, to about 122°; then to 145° and finally to about 160°.

After inversion is completed, the mash is run into the strainer. The subsequent operations of straining, fermenting, sparging, boiling, hopping, cooling, fermenting, storing, are carried out much in the same way as in the United States. There is, however, no separate chip-cask treatment, with its processes of fining, kraeusening or carbonating. After the beers are stored for some time, usually for six weeks or two months, chips are introduced into the storage cask and the beer is bunged, the secondary fermentation being depended upon to furnish the requisite life.

Malting. This is the process of preparing cereals, usually barley, for brewing purposes.

Barley is the favorite cereal employed, chiefly because the husk acts as an excellent filtering material in the mash-tun; its endosperm is readily modified and mellowed during growth, unlike corn; and it develops a sufficiency of enzymes during the malting process.

Oats, the only other cereal which retains its husk in threshing, contains large quantities of objectionable albumen, that preclude its employment.

[1] "American Handy-Book of the Brewing, Malting, and Auxiliary Trades," 1908, p. 1250.

COMPOSITION OF VARIOUS BEERS

	Specific Gravity	Alcohol by Weight	Alcohol by Volume	Extractive Substances	Proteins	Phosphoric Acid	Fixed Acid Lactic Acid	Original Extract	Analyzed by
American lager beers. Average of 14 samples...	1.0204	3.83	4.78	6.19	0.69	0.116	0.189	13.85	Doremus
Average of 222 samples of lager beers from all parts of U. S....	1.0164	3.85	4.81	5.79	0.62	0.095	0.124	13.49	Engelhardt
Average of 210 samples.....	1.0157	4.01	5.01	5.70	0.56		0.10	13.45	Wahl-Henius Institute
Domestic all-malt beer.....	1.0206	3.89	4.86	5.40	0.70	0.085	0.072	13.18	"
Actien Bry. Pilsen, Bohemian..	1.0137	3.60	4.50	5.08	0.397	0.100	0.054	12.28	"
Würzburger Bürgerliches Brauhaus, Bavarian..	1.0149	4.25	5.30	5.68	0.494	0.080	0.045	14.18	"
Stock ale in bottles, domestic...	1.0132	5.31	6.63	5.70	0.498	0.055	0.090	16.32	"
Dogshead bottling, Bass & Co., England.....	1.0064	6.11	7.60	4.30	0.525	0.060	0.054	16.52	"
American brown stout.....	1.0218	5.37	6.71	7.83	0.56			18.15	"
Guinness' extra bottled foreign stout, Dublin...	1.0136	6.29	7.86	6.15	0.75	0.108	0.243	18.22	"

In the United States, the systematic study of American barleys, with a view to their improvement, was begun in 1904 by the United States Department of Agriculture, and was fruitful of much new knowledge.[1]

The history of barley culture in the Western States of the Union may be dated from the settlement of German pioneers in the territory which is now the State of Ohio. In the Eastern States only local or Canadian barley was used up to about 1875, when the Manchuria barley, introduced into Wisconsin from Germany (about 1880), and thence spreading into Minnesota, Iowa, South and North Dakota, became the dominant type of the American market. The Bay Brewing type is mostly cultivated on the Pacific Coast, in California, Oregon and Washington; the White Club in Utah, Oregon and Washington; the Chevalier or two-rowed type, in Montana, California and the British Northwest.

The *barleycorn* consists in the main of the *husk*, the *germ* and the *endosperm*. The husk is mainly for protection, the germ contains the vital principle endowed with the faculty of growth, under suitable conditions, into the new plant, and the endosperm contains the bulk of the nourishment to sustain the germ until, in the natural order of things, the green leaves are sufficiently developed to assimilate carbonic acid from the air.

Through *germinating*, the endosperm of the barley is modified, thus becoming more porous as particles of starch, albumen and phosphates are made soluble by the action of diastase, peptase and lactic acid, and utilized by the germ as food in the form of amides, sugar and acid

[1] U. S. Dept. of Agriculture, Bulletin No. 124, Bureau of Chemistry, on "Study of American Barleys," by Leclerc and Wahl.

phosphates, while caramel is formed on the kiln in proportion to moisture contained at high temperatures.

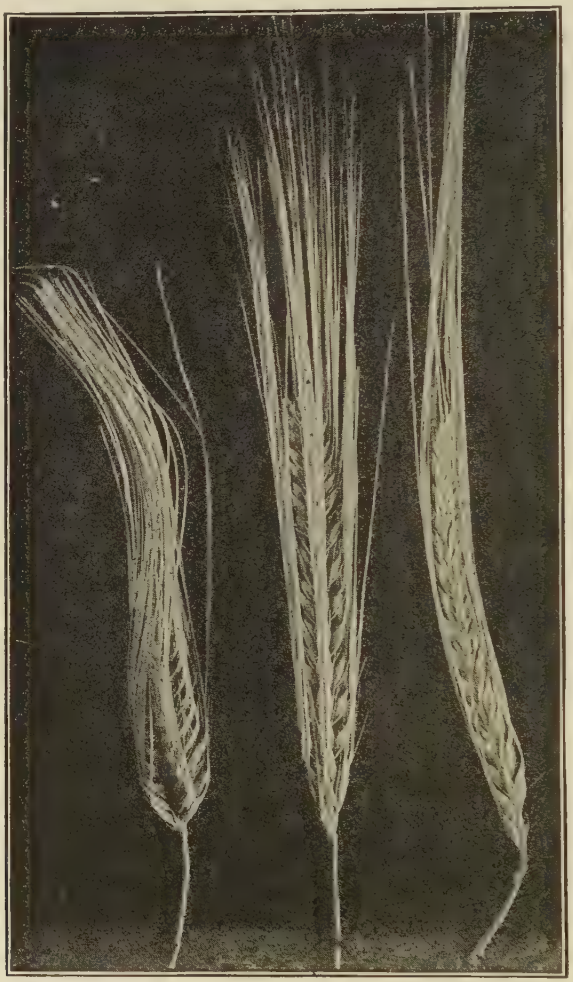

FIG. 353.—Barley Types: to the left, six-rowed (Utah Winter); in the middle, Two-rowed (Chevalier); to the right, six-rowed Drooping (Manchuria) or common.

During growth the germ of the barleycorn develops the *acrospire* or *plumula,* and the *radicle.* The former is that part from which develops the green blade which appears above the ground where barley is planted and eventually produces the stalk. The radicle sends out a number of shoots that develop into the roots of the plant and are commonly called *rootlets.*

In germination, the rootlets protrude at the germ end of the grain, while the acrospire, starting from the same end, grows up toward the

other end of the grain, keeping under the husk along tne back or solid side of the grain.

In malting, it is not allowed to reach the point of breaking out, the growth being checked suddenly by kiln-drying before the acrospire quite reaches the opposite end, experience having demonstrated that the most desirable condition of the endosperm coincides with that degree of development of the acrospire. For properties of malt, see " Brewing Materials."

Malting Operations. Broadly these embrace every manipulation from the moment the crude grain leaves the elevator or storehouse up to the time the finished malt is conveyed to the storage bin or to the hopper to be measured into the crusher mill of the brewery. In a more confined sense, as treated here, the term is applied only to the three main operations of steeping, germination and kiln-drying.

Growth. Germination as conducted on a smooth floor constructed of cement for this purpose, is the traditional method, the process being called " flooring," " growing," or " germinating." The modern methods, however, are based on artificial or forced aeration (pneumatic malting) either on a perforated floor or in revolving drums. Another important distinction is, that by the old method the work is almost entirely done by hand, whereas the improved methods may with much propriety be called mechanical malting, most of the work being done by machinery.

Floor Malting. The barley from the bins is loaded on the conveyor and carried automatically to the cleaning machine. The offal goes to feed dealers.

Steeping. From the cleaning machine the barley drops into the separator underneath. The different grades, two or three in number, go to the automatic scales, and then reach the steeping tank, which should be half filled with water. At first, the water should stand 1 to 2 ft. above the barley when the tank is full. The skimmings are floated off or skimmed off with a ladle. They go to a separate bin or trough, and are dried and sold for feed. Change the water twice the first day and once a day thereafter. Steep for about forty-eight hours, modifying for dryness of air, hardness and temperature of water, type and condition of barley, etc.

Germinating. The grain being fully steeped, the water is drained off at the bottom and the barley dropped on the malting floor; otherwise it is loaded on trucks and wheeled to the floor where the grain is spread and leveled to a heap or " couch " of about 8 to 10 ins. Here it is turned from time to time by hand shovels and its height gradually increased and again reduced according to conditions from about 14 ins. to 4 or 5 ins. The temperatures in the air should be about 50 to 60° F., in the growing malt couch about 75°, turning to prevent too high heats and to supply aeration. Growth takes about five days for barley of the Manchuria type and eight days for Bay Brewing and two-rowed types, like the Chevalier. When the endosperm has become mellow and the acrospire

is three-quarters up, the "green malt" is conveyed to the kiln which usually has two or three floors heated by open fire assisted by closed heaters; hard coal being smokeless, is commonly used for fuel.

Kilning. By a fan installed above the upper floor air is sucked through the malt together with the products of coal combustion. The temperature is kept at about 90° F. on the upper floor, and when hand dry, usually after twenty-four hours, the malt is dumped on the lower floor, where it is kept for about twelve hours at 120–130° F., where it is kept until practically dry, when it is heated to the final temperature of 150–155° F., for pale beers, 165–180° for darker beer, and up to 220° F. for beers of Munich character.

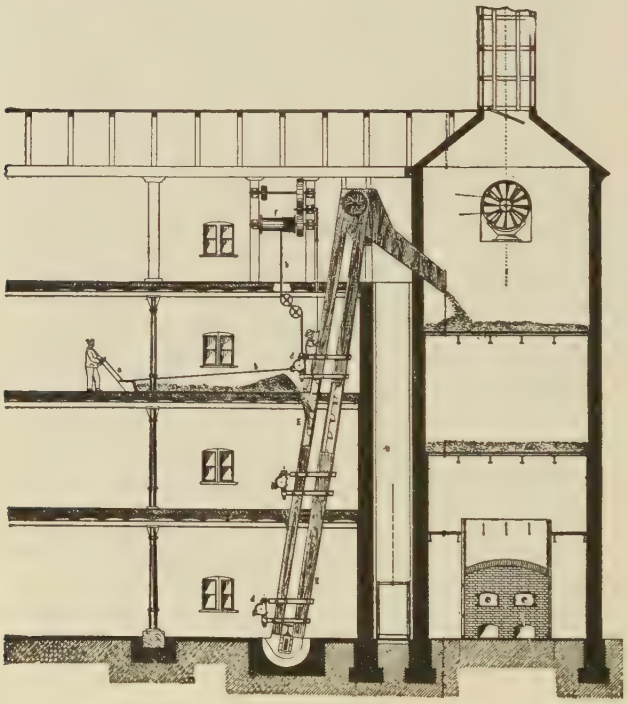

FIG. 354.—Floor Malting with Power Shovel and Bucket Elevator.

The Mechanical Malting or Automatic Pneumatic Systems. In this system malt is made by turning the same with machinery, or by the use of dumping floors, or other mechanical means.

The Compartment System. This system employs a box-shaped receptacle for holding the steeped barley during the growing period. Traveling across this receptacle lengthwise is a carriage supporting a number of revolving helices for the purpose of turning and loosening the growing barley. This carriage travels from end to end automatically, being propelled by rope transmission. The malting floor consists of perforated,

galvanized steel plates through which the attemperated air passes. The ventilation can be either downward or upward, or intermittent or continuous. The air first passes through the attemperators, which consist of a number of partitions having perforated zinc plates secured thereon. Between these partitions are located atomizers to spray the water on to the plates, thus effecting the cooling, and moistening to the saturation point, at the same time washing and purifying it, and equalizing the temperature. The water used returns to a tank, which has an overflow and skimmer. Here fresh water is added, and the water used over again. In cold weather the air used first passes through a series of steam coils, to be warmed, and then through the attemperator. Many plants are arranged so as to use part of the air over again, which effects a large saving in heating, and has given good satisfaction.

The moistening of the growing barley is done by a spray pipe attached to the machine and connected with a hose to the water supply. While being sprinkled, the malt is turned by the machine so as to moisten it uniformly.

The unloading of the compartment is done by a power scraper, which is so arranged as to run forward and backward, the operator only doing the guiding. The malt is scraped to the front of the compartment into a feeder, which feeds the malt into the conveyor underneath, then to the green-malt elevator, and then to the kiln.

In all other respects the treatment does not differ from that above described for the other methods of malting.

The floors are kept clean by scrubbing with brushes and the usual chemicals.

Drum Malting. The growth of the barley takes place in drums that are made to revolve by machinery whenever desired. The drums proper rest on four wheels in a frame connected to two shafts and revolved by means of worm gears; some are arranged so as to run at different speeds for different times and different conditions of the malt. The ventilation used in most cases is continuous.

The drum is turned about as follows: For the first three days, one full revolution every two hours; fourth day, every one and one-half hours; first half of the fifth day, the same; after which the drums are kept revolving for twelve hours, making one revolution in about forty minutes.

On the kiln the malt is dried the same as floor malt.

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CHAPTER XL

WINE MAKING

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Origin and Development. The origin of wine making undoubtedly dates back to prehistoric times. When for the first time some crushed grapes happened to be put aside in a vessel, nature itself transformed them into the first wine, and this result, so pleasing to the palate, most obviously invited repetition as well as attempts at further improvement.

From these crude beginnings the art of wine making has slowly developed, through the experience of centuries, to a high degree of perfection, nevertheless still remaining a merely domestic industry, the underlying principles of which were, as yet, entirely unknown. The cellar-master of old, seeing his wine undergo a renewed fermentation at the time when the vineyards blossomed, attributed this to a mysterious sympathy still existing between the vines and their offspring. His lack of knowledge is evident, but no less so his high esteem for the noble wine which he believed animated by some subtle form of intelligence and feeling.

During the last fifty years the researches of scientists such as Pasteur, Hansen and Wortmann, have led to a better understanding of what takes place during fermentation and ripening of wine. The old empirical methods have been tested in the light of modern biology and chemistry, and to-day, perfected and firmly established, the old art of wine making has developed into a rational industry.

But, whereas the modern development of most other industries has involved thorough centralization with the use of machines instead of hand-power, facilitating the handling of large quantities and ensuring uniformity of product, wine making in these respects has remained largely on the old domestic basis. Large wine-making establishments recording their annual output in hundreds of thousands or even in millions of gallons are found only where grapes are very abundant, as is the case in southern France and California, but the average wine maker of to-day still remains to a large extent the small wine grower who handles only his own harvest of grapes. He even finds it advantageous to grade his harvest according to quality, especially so, if he happens to be favored by soil or climatic conditions. The handling of large quantities on a truly industrial scale

is, therefore, still left to the wine merchant and to the manufacturer of sparkling wine who, by means of skillful blending, produce the standard types that meet the demands of the market.

The Grapes. The quality of a wine depends mainly upon the quality of the grapes from which it is made and the latter is determined by a number of factors such as variety of grapes, treatment of the vines, soil and its cultivation, climatic conditions and the degree of ripeness which the grapes are allowed to reach.

It is only where a suitable variety of grape is grown under especially favorable conditions as to soil and climate that the high grade wines can be produced. Under other conditions the identical grape variety may give a wine of a distinctly different character. The Riesling grape, when grown in California, is different from the Riesling that finds ideal conditions for its development in the temperate climate of the sunny hills along the Rhine, and the name Riesling on the label of a California wine therefore invites a comparison that cannot but result in adverse criticism. The wine growers of each territory, when selecting and developing those varieties of grapes that are best suited to local conditions, and modifying their methods accordingly, may gradually develop wine types of their own to be judged entirely upon their own merits.

It is important that the grapes be picked at the proper time which usually means when fully ripe. If picked at an earlier stage they give a must containing less sugar but richer in acids. For this reason early picking is sometimes resorted to in southern countries where the hot and dry climate tends to produce little acid and much sugar. Over-ripeness of the grapes is undesirable as it will cause them to shrink and their skin to burst laying open the juice to the dissolving action of rain and dew and offering breeding places to dangerous " disease " germs.

The weather during the picking is not without importance. Rain will, to some extent, dilute the must; heat will accelerate, while cold will retard the subsequent fermentation.

Stemming, Crushing and Pressing. After being gathered and carted to the winery the grapes are to be prepared for the fermentation as quickly as possible. Any delay is likely to detract from the quality of the resulting wine. If the production of white wine is intended, the grapes which may be either red or colorless, are crushed and pressed, only the juice (must) being fermented; if red wine is to be produced red grapes are stemmed and crushed, the whole pulp being filled into fermenting vats where the coloring matter is extracted during fermentation. In some cases the stems are left in the fermenting pulp but as a rule they are removed either before or after the crushing. The early removal of the stems is advisable, for they have a tendency to clog the pipes and flumes that are used for conveying crushed grapes and furthermore they impart an undesirable taste to the wine.

The device used for stemming may consist in its simplest form of a

wire screen, with meshes of a size to permit the grapes but not the stems to go through, over which the grapes are pushed by hand with a rake. Another device, intended for machine power, consists of a horizontal perforated cylinder in which a shaft with helically arranged arms revolves, thereby carrying the stems toward one end and causing the grapes to fall through the perforations. Where stemming is performed after crushing, the crushed grapes are dropped into a strainer in which there is a rapidly revolving set of narrow blades. These blades tear out the stems very completely from the mass of pulp.

The machine in which the grapes are crushed usually consists of a hopper feeding the grapes to a pair of adjustable grooved rollers revolving in opposite directions and with unequal speed. The purpose is to thoroughly open up all of the grapes without crushing the seeds from which undesirable substances would otherwise be extracted, whence the rollers are adjusted accordingly. Part of the must is often allowed to drain off from the crushed grapes by gravity alone and may be fermented separately as being superior to the rest of the must that is obtained by pressing.

The wine presses are mostly ordinary screw-presses, sometimes however hydraulic presses are used. The crushed grapes are spread in a uniform layer over the press-bed and subjected to a gradually increasing pressure. Too strong pressure should not be applied at once lest the yield be diminished. To insure the highest yield, it is necessary to loosen up the pressed residue once or twice and to re-press. As already stated the pressing of white wines takes place before, that of red wines after fermentation.

The Must. The grape juice is a watery solution, the main constituents of which are:

1. Sugar;
2. Organic acids;
3. Protein substances;
4. Flavoring substances;
5. Pectin and mucilaginous substances;
6. Mineral substances.

1. The sugar, during fermentation, is split up into about equal parts of alcohol and carbonic acid, and only very little sugar (less than 0.15 per cent) should be left in ordinary dry wines. A must containing 16 to 17 per cent sugar will produce a table wine with an alcoholic strength of 8 to 8.5 per cent by weight; musts containing less sugar produce the light ordinary wines, those containing more sugar result in the heavier high-grade wines.

2. The organic acids, chiefly tartaric and malic, although present in comparatively small quantities are very essential constituents of the must. The tartaric acid mainly occurs in combination with potassium as tartrate (bitartrate of potassium) which is precipitated to a large extent during the fermentation. A part of the acids is also consumed by the yeast and by certain bacteria which accounts for the fact that a wine has less

acidity than the corresponding must. The total acidity of must or wine is usually given as the apparent percentage of free tartaric acid.

To make a wine palatable its acidity must be in proper ratio to its alcoholic strength and palatefulness. A light wine without prominent flavor and body may appear fully harmonious as to taste with an acidity of only 0.4 per cent, but a heavier, highly flavored, wine would taste quite flat when possessed of this same acidity and may require as much as 1.0 per cent acidity to appear harmonious.

A must usually loses from 0.2 to 0.6 per cent in acidity during its transformation into wine.

3. The must can contain up to about 1 per cent of protein substances of which only approximately one-half remains in the wine, the rest being partly utilized as nourishment by the yeast, and partly precipitated during the fermentation.

4. The flavoring substances of the must upon which its quality largely depends are present in too small quantity to be isolated without great difficulty and we possess at the present time only scant knowledge of their chemical nature.

These flavoring substances increase during fermentation, the fermented must containing: 1. Those originally present in the must. 2. Others formed during the fermentation, probably mainly by decomposition of certain nitrogeneous substances (amino-acids) contained in the must, and 3. The specific flavoring substances produced by the different varieties of yeast irrespective of composition of the must (esters and aldehyde).

5. The pectin and mucilaginous substances causing the thick consistency of the must are practically all precipitated during the fermentation as they are insoluble in dilute alcohol.

6. In a normal must is found from 0.3 to 0.5 per cent of mineral substances (ash) the amount of which considerably decreases during the fermentation owing to the precipitation of potassium in the form of tartar.

The wine maker tests his must to determine approximately the sugar and acidity of an average sample. The sugar is determined by means of areometers such as Oechsle's must scale, indicating how many grams one liter of must weighs more than one liter of water, or Balling's saccharometer indicating the percentage of solids in solution. Degrees Oechsle divided by five, or per cent Balling multiplied by $\frac{5}{6}$ gives the sugar content in per cent of an ordinary must with sufficient accuracy for practical purposes. The acidity is measured by titration with standardized alkali solution. Knowing the ratio of sugar to acidity the wine maker is in a position to carry out the subsequent operations with a view to either checking or facilitating the decrease in acidity according to the requirements.

A direct correction as to composition may also be found desirable. If lacking in acidity the must can be corrected by the admixture of less ripe grapes or by the addition of tartaric acid. The addition of gypsum, which is sometimes used, especially in making red wines, has a similar

effect, the gypsum reacting upon the tartar so as to form insoluble calcium tartrate and bisulphate of potassium which latter substance, unlike the tartar, remains dissolved in the wine. This method, the so-called plastering, can only be used to a limited extent, since the laws of most wine producing countries fix a maximum limit for sulphates contained in unadulterated wine.

If the must is too rich in acids, the acidity can be reduced by dilution with water and the proper sugar content eventually restored by addition of pure cane or grape sugar. This process, known as gallizing, is used to some extent in northern countries, especially for white wines, and is generally considered legitimate, provided it is carried out so as to actually improve, or to render marketable the product and not with a view to unduly increase its quantity. The process of improving must by adding sugar and neutralizing the excess of acidity (usually by means of chalk) is known as chaptalizing.

The Fermentation. When left to itself the must will soon begin fermenting. It grows quite turbid, gas bubbles rise to the surface, the temperature rises and the viscosity and specific gravity decrease. At the same time the sweet taste gradually changes into a vinous one and a distinct flavor develops Toward the end of the fermentation the turbidity gradually disappears and the completed fermentation leaves the young wine in a limpid state on top of a heavy sediment.

These changes are brought about by certain microscopical plants that are always present on the skins of ripe grapes. Among them the yeasts which cause the alcoholic fermentation, splitting up sugar into alcohol and carbon dioxide, are desirable and indispensable, while others such as mycoderma and various bacteria are undesirable disease germs.

Between the microörganisms a struggle for life goes on in the must, each one striving to utilize the nourishment on hand for its own growth and producing substances that are injurious to its competitors. By far the most important task of the wine maker is to assist the yeast in this struggle by offering it the most favorable conditions for its activity. His aim is to make the yeast ferment the sugar as completely as possible which not only means little nourishment left for other organisms but also a high percentage of alcohol prohibiting their growth. Incomplete fermentation on the other hand results in a weak and unstable wine subject to a variety of undesirable changes.

The Wine-yeasts. The alcoholic fermentation of the must is caused by small, usually unicellular budding fungi, mostly belonging to the different varieties of saccharomyces ellipsoideus. Their principal breeding places in nature are the ripe juicy fruits where they multiply abundantly during the fall. Some of them penetrate with the rain to a certain depth into the soil, where a sufficient number keep alive over winter to repopulate the fruits of the following year, to which they are carried by insects, rain-splashes or the wind. Their perpetuation is facilitated by their power

of forming spores, small resistant cells appearing under certain conditions within the vegetative cells.

The yeast cells contain an enzyme, the zymase, which in contact with dissolved sugar transforms it into alcohol and carbon dioxide. This fermentation proceeds most satisfactorily at medium temperatures, the yeast becoming temporarily inactive at a few degrees above the freezing-point of the water and permanently weakened at about 100° F. Even the most vigorous yeast can only produce about 13 per cent of alcohol by weight and this only under exceptionally favorable conditions.

Besides the main products of the alcoholic fermentation smaller quantities of glycerol, succinic and lactic acids, aldehyde and fusel oils are also produced by the yeast during fermentation. Apart from the glycerol, that may—as far as our present knowledge goes—be derived from the sugar, the other by-products have recently been shown to originate from amino-acids (e.g., succinic acid from glutamic acid and amyl-alcohol from leucine) the nitrogen being utilized by the yeast in the form of ammonia for building up the protein of its own body. In all probability flavoring substances are formed by a similar process from other amino-acids, the primary products being various alcohols and acids, which during the ripening of the wine are further transformed through oxidation and esterification.

Pure Cultures of Yeast. Many different wine-yeasts have been isolated and studied. They differ, more or less, not only morphologically but also as to the rapidity and completeness with which they ferment sugar, as well as to their power of decreasing the acidity and as to the strength and fineness of the flavor they produce. This naturally led to the use of selected pure cultures of yeast for the fermentation of wine. Such cultures are kept in stock and furnished by especially equipped laboratories. In the wineries they are first propagated in a suitable quantity of boiled and cooled must, which is allowed to come into vigorous fermentation before being added to the bulk of the ordinary must. The addition of only $\frac{1}{2}$ per cent suffices to secure the predominance of the selected yeast.

The use of selected pure yeast results in better control of the operations, a cleaner taste and flavor and an earlier ripening of the wine. A specific flavor is also to some extent obtained, according to the yeast variety employed, but many exaggerated claims have been made in this respect by too ardent advocates of the pure cultures. Indeed the use of pure culture yeast in vinification is practically without any importance for the reason that it implies a prior sterilization of the must, which is costly, and above all detracts from the flavor of the wine. If wines are to be re-fermented pure cultures are particularly useful, and special advantages are also derived from their use in the manufacturing of sparkling wines.

Undesirable Micro-organisms of the Must. Among the micro-organisms occurring on the ripe grapes together with the genuine wine-

yeasts the most important are *saccharomyces apiculatus, mycoderma vini,* and acetic acid bacteria.

The small lemon-shaped cells of saccharomyces apiculatus are often present in sufficiently large numbers to start the alcoholic fermentation of the must, but they are soon superseded by the more vigorous saccharomyces ellipsoideus. They produce a less desirable flavor and one of the purposes in using pure cultures of yeast is to restrict their activity.

Mycoderma vini forms a film on the surface of the wine and consumes alcohol, transforming it into carbonic acid and water by oxidation. Though it may not be directly harmful, it thereby renders the wine less resistant against the attacks of other disease germs.

The acetic acid bacteria, minute rods that are often united in long chains, produce acetic acid from alcohol and are, therefore, very dangerous disease germs. As little as 0.1 to 0.15 per cent of acetic acid makes a wine decidedly " pricked " and with a content of 0.25 per cent most dry wines may be considered undrinkable. Exclusion of the atmospheric air protects against the growth of these bacteria.

Other diseases (turbidity, unclean, bitter or sour taste, ropiness, etc.) are occasionally caused by other bacteria, especially in the lighter grades of wine or in wines that have not been completely fermented.

White Wines. The white wines are produced by fermentation of grape juice that has been separated from the skins, seeds and stems. A fermentation of this kind offers comparatively little difficulty, but the resulting wine is decidedly more delicate than those fermented on the skins, whence its subsequent treatment and proper ripening require greater care.

The fermentation is usually carried on in casks that are filled to $\frac{7}{8}$–$\frac{9}{10}$ of their capacity with grape juice and the bung hole is closed so as to allow the carbon dioxide to escape but no air to enter. The duration of the fermentation is from one to two weeks, depending on the temperature, which usually is 60–70° F., and on the quantity of yeast originally present. In California wineries temperatures of 85–95° F. are usually employed. The temperature is controlled by cool water coils or, according to the latest experience, simply by using thin-walled cement fermenting vats, which radiate heat so rapidly that they automatically control fermentation temperatures. At the end of the fermentation the yeast sediment is sometimes stirred up again in order to facilitate the complete splitting up of the sugar and the reduction of acidity. Only where extremely favorable conditions (temperature) prevail, as in California, fermentation does not stop, when the wine still contains 1–4 per cent of sugar. In the following spring and summer a secondary fermentation sets in in such wines.

After the fermentation is over the wine is drawn from the lees into another cask in which some sulphur has been burned to check the further activity of micro-organisms. This cask is completely filled, tightly bunged

and as a rule kept at a temperature of 50–55° F. Before the rising temperature of the following spring causes a slight revival of the fermentation, the wine is racked off from the sediment once more, and this process repeated several times during the subsequent ripening period. At each racking an oxidation takes place, resulting in precipitation of certain albuminoids and further development of the flavor, until finally the wine has become sufficiently stable to be filled into bottles.

In the ordinary grades of wine this ripening is generally more or less forced by means of a more thorough aëration during the racking, artificial clarification (filtration or use of finings), and eventually pasteurization. Of late Hertzian waves are utilized for aging wine.

The simplest form of wine filter is a cylindric or conical linen bag into which the wine is poured and returned until it runs clear. The more modern filters are closed so as to protect the wine from the air. Their filtering material is either pure cellulose or paper-pulp (the latter enjoying the greatest popularity in this country) packed into one or more filtering chambers or especially prepared asbestos-wool stirred up with a smaller part of the wine and pumped into the filter where it deposits as a uniform layer on walls formed of fine wire screens. Asbestos screens are very efficient; they practically give a sterile filtrate.

Finings are added to the wine in order to produce a very finely distributed sediment of higher specific gravity which will gradually settle to the bottom, carrying with it all suspended solid particles. For fining white wines isinglass is commonly used. It is soaked in water and at last in wine until nearly transparent and then vigorously beaten with some more wine eventually under addition of tartaric acid, filtered through linen and thoroughly distributed into the wine in the cask. One ounce of isinglass can generally fine 200–500 gallons of wine within 8–10 days. Casein and skimmed milk are often employed with great advantage for fining defective wines.

Red Wines. The red wines derive their characteristics from being fermented in contact with the skins of red grapes, from which they extract not only coloring matter but also a variety of other substances, especially tannins. Normal red wines contain from 0.1 to 0.3 per cent of tannin while the percentage of this substance in white wine does not as a rule exceed 0.02 to 0.04 per cent. Owing to this high content of tannin the ripening of red wines is a comparatively easy matter once the fermentation has been properly carried through, but the presence of the skins at the fermentation on the other hand gives rise to several difficulties during this process.

The carbon dioxide carries the skins to the surface where they form the so-called cap, which must be pushed down repeatedly in order to insure proper extraction and uniformity of fermentation. Closed casks are therefore less suitable and in the open tubs, which are generally used, there is great danger, however, of acetification owing to the free exposure of

the cap to the air. To overcome these difficulties the fermenting tubs are often provided with removable grates that are held in horizontal position about 5 ins. below the surface of the liquid thus prohibiting the skins from rising to the surface. To insure proper uniformity the wine is drawn off at intervals from the bottom of the tubs and pumped back to the surface.

The temperature during fermentation of red wine is usually 65 to 85° F. As red wines are mainly produced in southern countries it is often difficult to prevent the temperature from rising too high, a considerable amount of heat being generated by the decomposition of the sugar. Too high temperature not only facilitates the growth of various bacteria but also prevents the yeast from completing the fermentation, the result being a wine of poor quality ("stuck wine") and easily subject to further deterioration. Artificial cooling is therefore often resorted to, water being circulated through cooling coils in the tubs or the wine being pumped through enclosed coolers.

After being fermented the red wine is drawn off into casks, which, however, are only sulphured in exceptional cases, because most red wines do not need this protection and would be more or less bleached by the sulphurous acid. Red wines are ripened in practically the same way as white wines but less time and fewer rackings are required to render them sufficiently stable for bottling.

The red wines are mostly fined with gelatine or white of egg. The gelatine is soaked in water overnight, dissolved in wine by gentle heating, cooled, stirred up with some more wine and added to the cask. One ounce of gelatine is required for 50–120 gallons of wine. Whites of eggs are often used to fine the better grades of red wine, one white for every 8–12 gallons. They are first beaten to a foam, pressed through a heavy linen, and then stirred up with some of the wine before being added to its bulk.

Sweet and Dessert Wines. The white and red wines referred to above are all dry, i.e., practically all of their sugar having been fermented. The sweet wines and the dessert wines on the other hand contain unfermented sugar besides a high or even very high percentage of alcohol. The typical sweet wines such as "Auslese" rhinewine, sauterne, or tokay contain much sugar, but their alcohol is produced by fermentation and consequently does not exceed 13 per cent by weight. The dessert wines such as port, sherry, madeira and malaga are less sweet but generally contain from 15 to 20 per cent by weight of alcohol, part of which has been artifically added.

The "Auslese" wines and sauternes are produced from grapes attacked by a certain mold, *botrytis cinerea,* which finds favorable conditions for its growth in a foggy, cool climate without too much rain. It causes the grapes to shrink and to partly dry up; the must being accordingly more concentrated and possessed of a peculiarly fine flavor. The fermentation is carried out with a view to produce enough alcohol to prevent further

changes, but since sugar is left unfermented these wines are prone to after-fermentation, and as a rule need heavy sulphuring to become stable.

In certain territories the dry and warm climate allows the grapes to dry up similar to raisins before they are picked. These yield a very concentrated must. The tokay wines of Hungary are made from such grapes, extracted with normally fermented dry wines and pressed. Imitated tokay is made in a similar way from ordinary dried raisins or from must concentrated by boiling in vacuo.

The various dessert wines contain more alcohol than can be produced by fermentation. An addition of alcohol is therefore necessary, and is often combined with an addition of condensed must or sugar. The alcohol may be added either at the end of the fermentation or at an earlier stage, in the latter case preventing part of the sugar contained in the must from being fermented. The addition is often made step by step, part of the total amount required being added at each racking and thoroughly mixed with the wine. During the ripening period the dessert wines are kept at a comparatively high temperature and freely aerated. This results in the development of the peculiar flavor known as madeira and sherry flavor.

Sparkling Wines. The sparkling wines are produced from either red or colorless grapes, the juice alone being fermented as usual for dry white wines. After being drawn off from the lees the wine is racked once more, a too high content of albuminoids being eventually decreased by an addition of tannin. The wine is blended in large vats or casks with a view to produce a uniform product from one year to another, and enough sugar solution is added so that a pressure of about 5 atmospheres (73.5 lbs. per sq. in.) can develop during the subsequent fermentation in bottles. Furthermore a culture of selected pure yeast is often added, and the wine is then bottled and corked, preferably in the spring, because the rising temperature facilitates fermentation. When bottled the wine has a temperature of 65–72° F., but the bottles are kept at about 50° F., when the fermentation has started. This temperature must be kept as constant as possible to avoid breakage. The duration of the bottle fermentation varies from one-half to two years. When the proper pressure is reached the bottles are placed in a slanting position on special stands, their necks being a little lower than their bottoms. A short shaking and turning movement is imparted to them once a day during about six weeks while they are gradually raised to a vertical position neck down. In this way the yeast sediment is carried down on the cork, leaving the wine entirely clear. This process can be greatly facilitated by the use of a proper variety of yeast; i.e., one combining a strong fermenting power with a tendency to grow in larger clusters.

The bottles are now taken to the uncorking room and eventually cooled to bind the carbon dioxide more firmly. The uncorking requires a good deal of skill. The operator holds the bottle in a slanting position and gradually loosens the cork until it is thrown out by the pressure together with the

whole sediment. Especially practicable is the method of Walford, who puts the neck of the inverted bottle in a glycerol bath of 4° F. In a short time the lower portion in the neck is frozen and forced out as a plug on opening the bottle. At the same instant the bottle must be turned upright and preliminarily closed. The " dosing " of champagne is performed by adding some sugar dissolved in wine before the bottles are finally corked, the quantity varying greatly according to the requirements of the trade. The sugar solution is thoroughly distributed by shaking and the bottles preferably kept in stock for some time before being consumed in order that the taste be more harmonious and the carbon dioxide more permanently bound.

Imitation champagne is made by saturating white wine with carbonic acid under pressure in a suitable apparatus, but such sparkling wines are generally lacking in life and, when poured into the glass, do not show the same permanent sparkling as those made by the slow process of bottle fermentation.

Diseases and Defects of Wine. The biological, chemical and physical processes involved in vinification not always progress in the desired direction, thus giving rise to various diseases and defects of wine. Diseased wines finally spoil completely if no preventive measures are taken in time, while defective wines remain potable, but possess an " off " flavor and taste. Most diseases are caused by micro-organisms. Particularly prone to diseases are wines derived from must, which were prepared from diseased (rotten) grapes. Pasteurization affords the best protection, but is not always applicable, especially not with quality wines, on account of its detrimental effect on flavor and taste. Wines in bulk are usually pasteurized at 175° F. (80° C.); with bottled goods 150° F. is the maximum temperature permissible. In both cases the time of exposure to the maximum temperature is very short, hardly exceeding two to three minutes. In many cases troubles may be remedied by filtration, combined with fining (using charcoal, gelatin, tannin, casein, milk), aëration and heavy sulphuring; in very severe cases re-fermentation (with pure culture yeast) is the last means resorted to. Following are enumerated the most common diseases and defects of wine:

Acetification (the worst of all, caused by various bacteria).

Mousy taste (developed in wines stored together with partly autolized yeast at too high temperatures).

Film formation (caused by certain yeasts).

Lactic turn (effected by numerous varieties of lactic bacteria).

Ropiness (caused by slimy fermentation due to certain anaerobic organisms).

Bitter taste (due to oxidation of tannin; rarely met in white, but frequently in red wines, especially when the grapes were infested with botrytis and penicillium).

Discoloration (due to oxidation with the aid of oxidases of substances

extracted from skins, kernels and stems or to the presence of an excessive quantity—over 0.003 per cent—of iron).

Clouding (turning) of finished wines (due to suspended organized matter—bacteria, etc.—or to precipitation of unorganized substances due to overfining or unproper blending).

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CHAPTER XLI

DISTILLED LIQUORS AND INDUSTRIAL ALCOHOL

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In the two previous chapters on "Brewing and Malting," and "Wine Making," the preparation of beverages was described, the alcohol content of which, with the exception of fortified wines, was obtained solely by the activities of microscopic plants, viz., yeast cells. The craving for alcoholic stimulants stronger than beer and wine led to the concentration of the alcohol contained in fermented grain mashes or wines by a process termed distillation.

Although the ancients knew of this process, the oldest records of its application for obtaining concentrated alcohol show that Arabian doctors used the latter for medicinal purposes as early as the tenth century. Up to about the fifteenth century, the production of many varieties of distilled or spirituous liquors was mainly carried out by the monks, who zealously guarded the secret, as is done even to-day in some of the monasteries famous for the exquisite liqueurs and cordials that they prepare. From about the fifteenth century on, distilling became better known among the people, at first being a household practice. When laws were passed by some governments, placing a tax on distilled spirits, and later forbidding distilling operations unless they were under government supervision, an infant industry soon developed. It is thus a comparatively easy matter to trace the history of the development of alcohol distillation from the laws made by various governments, regulating the tax and restrictions imposed upon the manufacture of distilled liquor for drinking purposes or of alcohol for employment in the technical arts. The severity of such laws was frequently protested against by the people. Even in the history of the United States there is an instance of this kind, which occurred in Western Pennsylvania in 1792 to 1794, when the new excise regulation for whiskey caused such a storm of protests, supplemented by violence, that President Washington was compelled to call out the militia to quell this so-called "Whiskey Insurrection."

Distilled Liquors. Distilled liquors differ greatly in flavor and general character, being influenced in these respects by the materials and the methods employed in their production. Their names vary according

to the nation producing them. Among the best known distilled or spirituous liquors are:

1. *Whiskey.* Made from malt and unmalted cereals in the United States, England, Scotland, Ireland, and Canada.

2. *Kornbranntwein.* Prepared from malt and rye, sometimes maize. Produced in Germany.

3. *Schnapps,* Is much consumed in Germany, also some of the neighboring European countries. Represents diluted rectified alcohol, obtained chiefly from potatoes. It often is flavored or sweetened according to the desired taste.

4. *Brandy.* Obtained generally from grape-wine, but also the fermented juice of many fruits. Prepared chiefly in France and the United States.

5. *Gin.* Produced from malt and usually rye or barley. Manufactured chiefly in Holland, but also in England and the United States.

6. *Rum.* Made from molasses in the West Indies and other sugar-cane-growing vicinities.

7. *Slibowitz.* Produced from the prune-type plum. Used commonly in Austria and some of the Balkan States.

8. *Arrack.* Prepared from palm-wine, rice and molasses. Produced in Siam, East India, Java, and also Jamaica.

9. *Vodka.* Made from rye and barley malt. Potatoes or maize also are sometimes used instead of rye. Is the common liquor of Russia.

10. *Cordials or Liqueurs.* Manufactured chiefly in France, Germany and the United States.

Before describing the manufacture of the various types of distilled liquors, a few remarks regarding the most important constituent, the alcohol, are necessary.

Ethyl or Fermentation Alcohol. Ethyl, grain, or fermentation alcohol is obtained by the fermentation of sugar solutions, under which heading the mashes from the saccharification of starch-containing materials are included. Besides ethyl alcohol, small amounts of higher alcohols, such as amyl, propyl and isobutyl alcohols, are produced during fermentation. These are more or less undesirable in distilled liquors that are used for drinking purposes; hence most distillers remove them by rectifying and refining the distillate, also by filtering it through crushed bone-black or charcoal.

In its absolutely pure form ethyl alcohol has a specific gravity of 0.7935 at 60° F. Many authorities differ slightly on this subject and a specific gravity of 0.7938 is mostly used in various tables. Ethyl alcohol is a limpid, colorless liquid that possesses a pungent taste and a vinous, agreeable odor. It is miscible with water in all proportions.

Proof-spirit. Although the correct and scientific manner of designating the alcoholic strength of a liquor is to state it as *per cent by weight,* the per cent by volume is generally employed, and in England and the

United States still more the term *proof-spirit*. This is the old-fashioned way of expressing the amount of alcohol of spirit, and unfortunately has survived to the present day in excise regulations and in the trade.

According to the old English law, the term proof-spirit, as used for excise purposes, designates an alcoholic liquor that weighs exactly twelve-thirteenths of the weight of an equal bulk of water, at a temperature of 51° F. The specific gravity of such proof-spirit at a temperature of 60° F. is 0.9198. It contains 49.24 per cent alcohol by weight and 57.06 per cent by volume. Spirits weaker than proof are designated U. P. or under-proof, and stronger than proof as O. P. or over-proof.

In the United States the proof-spirit is considerably lower than in England, being only 42.52 per cent alcohol by weight and 50.0 per cent by volume. The instrument adopted by the United States government for ascertaining the strength of spirit is the Tralles hydrometer, which indicates the per cent alcohol by volume at 60° F. Tralles' alcohol had a specific gravity of 0.7946 at 60° F., or in other words contained 0.25 per cent water when compared to alcohol of a specific gravity of 0.7938.

Distillation. This process, as applied to alcoholic liquors, consists of evaporating or volatilizing the alcohols obtained by fermentation and then passing the vapors to a condenser, in which they are cooled and condensed. The apparatus used in distilleries varies from the simplest form of a copper still and worm condenser to the modern fractionating type. Primitive pot-stills often are employed by some distillers who claim that a certain characteristic flavor of their whiskey can only be obtained in this way. Such are also used for illicit distilling, namely, making so-called " moonshine " whiskey. There are numerous types of modern stills which allow a continuous combined distillation and rectification and two of the most commonly employed ones are described in Chapter L.

Rectification and Refining. The first portion of alcohol distilled from the fermented mash or liquor is a crude milky spirit. It contains more or less undesirable alcohols, collectively termed fusel oil and consisting chiefly of amyl, propyl and isobutyl alcohols. The vapors of these are considerably heavier than those of ethyl alcohol. In distilling practice they are therefore collected in a special vessel, from where the condensed liquid can either be separated from the distillate proper, or it can be run back into the still.

The last portion of the vapors obtained from the still contains comparatively little alcohol. The excess water to a great extent is held back in the " doubler," or rectifying vessel, of which one, two, or sometimes even three, are placed between the still and the worm in the older apparatuses.

When very concentrated alcohol, namely, rectified spirit, which contains about 95 per cent pure alcohol, is desired, the rectification must be carried out very thoroughly, which can easily be done in the modern stills.

The alcoholic distillates are also sometimes purified by passing them through a bed or thick layer of ground charcoal or bone-black. This is done to remove more completely the objectionable fusel oil or any other oils or ethers volatilized during distillation. This practice is mainly confined to certain types of whiskey and to rectified spirits.

Under the term whiskey is understood the potable spirit distilled from fermented mashes, made either from malt alone or a mixture of malt and unmalted cereals. The latter usually are barley, rye, maize (Indian corn), oats and wheat. The malted cereals generally are barley malt, rye malt, wheat malt, and in a few instances oat malt.

Genuine whiskeys are of three different types: American, Scotch, and Irish. They differ vastly in flavor, body and color. Space will not allow describing in detail the process of manufacture of each of the whiskeys, and for this reason only a general description can be given.

American Whiskey. In the United States two distinctive types of whiskey are produced, namely, rye and Bourbon. The grain used for manufacturing rye whiskey is a mixture of rye malt or barley malt and unmalted rye. Bourbon whiskey was originally prepared in Bourbon County, Kentucky, and is made from barley malt or wheat malt and maize (Indian corn).

Some whiskeys are designated as "sour mash" whiskeys. In their preparation, the raw material is "scalded," or mashed with spent beer, namely the liquid portion that remains from the distillation of a previous mash. In distinction, a "sweet mash" whiskey is one where fresh water is employed.

The quantity of malt used amounts to from 10 to 15 per cent of the total weight of the materials in the lower grades of whiskeys, and from 20 to 50 per cent in the better grades. Few whiskies are made from malt alone.

The taste and general character of the different whiskeys vary according to the materials employed, their quality—with special reference to the malt—and to the methods of mashing, fermentation, distillation, and aging of the distilled liquor. The finer the quality of the materials and the higher the percentage of malt the better will be the taste and flavor of the product.

Malting. The same general principles of malting, as outlined under the chapter of "Brewing and Malting," are carried out to a great extent when manufacturing distillers' malt. Special attention is given so that the resulting malt is of the highest possible diastatic power or strength, since the yield in gallons of spirit is materially affected thereby. Inferior diastatic malts give rise to difficulties in the saccharification of the starch contained in the unmalted cereal, which means a loss of alcohol. For that reason, the malt should not only be prepared from the best grade of six-rowed barley, wheat, or rye, but during the growing and kiln-drying periods, all precautions must be observed to minimize the danger of a

weakening effect upon the diastase produced by the germination of the grain.

The acrospire or leaf of the sprouting grain is usually allowed to grow to the length of the kernel itself at low and very uniform temperatures. The sprouted grain is then kiln-dried or cured by passing large volumes of of air through it. During the first twenty-four hours, the temperature of this air should not exceed 90° F. and in the next twenty-four hours more heat is applied until the temperature during the last five to six hours is about 120 to 130° F. Higher kilning temperatures, especially during the first twenty-four hours, will greatly reduce the diastatic strength of the malt.

Unmalted Cereals. Indian corn, or maize, is most commonly employed for American whiskeys. White flint corn is needed for the best grades. Rye is mainly used for producing whiskey bearing this name, whereas wheat has generally been too expensive in recent years. The employment of potatoes has never found favor among American distillers.

All of these cereals should be well matured in the field and thoroughly dried before storage in the bin. The taste and odor should be clean and agreeable, and under no circumstances should it be mouldy, sour or rancid.

Mashing Operations. In the manufacture of American whiskeys, the mashing operations consist of:

1. Pastifying the starch of the unmalted cereals.

2. Changing the pastified starch and that of the malt to fermentable sugar (maltose). The more maltose obtained, the higher will be the yield of alcohol.

The pastifying of the starch of the unmalted cereals is accomplished by mixing 18 to 26 gallons of water—temperature about 140° F. per bushel—usually taken at 56 pounds—of the finely ground cereal, in a suitable vessel. A small amount of malt is generally added in order to assist in the pastification of the starch, but the quantity depends upon the total percentage of malt used in the preparation of the whiskey.

Most small distilleries employ a wooden or iron cylindrical tank for both the pastifying of the starch and the final inversion of the mash. In larger plants a special vessel, termed cooker or converter, in which the mash can be boiled under pressure, is available. Such pressure cookers allow a better pastification of the starch, since the raw cereal mash can be heated under pressures corresponding to temperatures of 250 to 300° F. In that case the mash-tank proper is a separate vessel.

After adding the ground grain to the water, the mixture is agitateed by means of a stirring device and gradually heated to boiling by live steam. In open cookers, the mash is boiled for one hour, or longer, and as soon as the starch has been properly pastified it is cooled by adding cold water or by passing cold water through a coil situated in the tank. When the temperature has been reduced to about 150° F., the finely ground malt is added, lowering the temperature of the entire mash to about 140° F.

After mashing at 140° F., for one-half hour or longer, the mash is heated to 150 to 155° F. by means of live steam. Mashing operations are continued for a short time and the mash then cooled to 66 to 72° F., either by means of the cooling coils in the mash-tank or by pumping the mash through a double-pipe cooler.

Fermentation. The almost completely saccharified mash is now ready for the addition of the yeast in order to induce fermentation. The liquid portion generally contains 12 to 13 per cent of soluble substances, of which almost 90 per cent is sugar (maltose). Since the diastase was not entirely destroyed during the mashing operations, it still acts upon any uninverted starch and certain types of dextrine during the fermentation period, thereby, changing them into fermentable sugar.

During the summer months the mash is cooled to about 66° F. and in winter to 72° F. As soon as the yeast becomes active the temperature rises and as a rule is allowed to go up to 88–90° F. but not higher. The temperature of the fermenting mash is held at about 90° F., which is accomplished by circulating cold water through attemporator coils with which the fermenters are equipped. In three and at the utmost four days the fermentation is completed and the fermented mash is ready for passing to the still.

Distillers' yeast is a higher attenuating, top-fermenting variety of *Saccharomyces Cerevisiæ.* There are numerous types. The many generations that they have grown in distillery mashes caused such yeasts to become acclimatized for obtaining a quick, most complete fermentation of the sugar. In recent years, *pure culture yeasts*, propagated according to the Hansen single-cell method, have been introduced extensively. The types selected were such as had been found in practice to give especially high alcohol yields.

The condition of the yeast at the time of adding it to the cooled mash is of vital importance. The individual cells should be young, vigorous and in a very active state of reproduction. The yeast is prepared by taking a small amount reserved from a previous fermentation and propagating it in a small special mash made from either barley or rye malt alone, or together with unmalted rye, barley or wheat. As a rule this special mash amounts to about 5 per cent of the volume of the big mash.

The most common practice is to use equal weights of barley malt and ground rye. The latter is scalded with water of about 170° F. After stirring for about ten minutes, the ground malt is run in and the mash held at a temperature of about 150° F. for two hours. The saccharometer indication of the liquid portion of this mash should be 22 to 25 per cent Balling.

The mash is now cooled to 118–120° F. and by allowing it to stand at this temperature for forty to forty-eight hours, a spontaneous souring, due to the development of lactic acid bacteria, occurs. The addition of about 3 per cent of a pure culture of mash lactic acid bacteria (*Bacillus*

Delbrückii) will effect the desired souring in eighteen to twenty-four hours, and this method is now being introduced in many distilleries.

After this mash has become sour, it is heated to 170° F. and held at this temperature for about twenty minutes in order to kill the lactic acid bacteria. The mash is next cooled to 85° F. by circulating cold water through the attemporator coil. A small amount of yeast is now added and when fermentation sets in, the temperature is slowly reduced to 80° F. As soon as the saccharometer indication has decreased to 7 or 8 per cent Balling, the fermenting mass is run into the cooled big mash.

The employment of this souring process by the action of lactic acid bacteria not alone adds to the peculiarity of flavor of the whiskey, but also is a desirable safeguard against the development of foreign microorganisms during fermentation, especially acetic acid bacteria, which produce acetic acid at the expense of the alcohol. The mildly acidified main mash also allows a more vigorous and quicker fermentation.

Distillation and Storage. As soon as the fermentation is complete the liquor is brought to the still and the alcohol distilled. After distillation, the spirit is stored in heavily charred oak barrels. Such charred casks impart color to the whiskey and aid in the process of maturation. During the latter period the whiskey is stored in bonded warehouses, from which it cannot be removed until the government tax has been paid. The latter is $1.10 per proof-gallon. The entire manufacture and storage of the whiskey is under the supervision of government officials, and no steps can be taken without notifying the revenue officer, located at the distillery.

Scotch Whiskey. Two different types of whiskey are made in Scotland. The one that is the characteristic Scotch whiskey is made from barley malt, and is usually termed pot-still whiskey, owing to the old-fashioned style of still used in its distillation. The other type is called patent-still, or grain whiskey. It is made from barley malt and unmalted cereals, mostly corn imported from the United States. Rye and oats also are sometimes used.

The genuine Scotch whiskeys are characterized by a peculiar smoky flavor and taste, which originate from the malt. This is due to the employment of various kinds of peat as fuel for curing, namely kiln-drying, the malt. This peculiarity distinguishes the genuine Scotch whiskeys from all other types. They are generally stored about five years, or longer, during which time the whiskey acquires a rich, mellow taste and improves greatly in flavor.

The patent-still whiskeys lack this smoky flavor and taste. They are more similar to some of our American whiskeys, both as to the general methods of manufacture and also as to taste and flavor.

Irish Whiskey. Most of the Irish whiskey is of the pot-still type. It is usually prepared from 30 to 50 per cent barley malt, the remainder being rye, barley, oats, wheat or a mixture thereof. The malt is not

peat cured and the resulting whiskeys have a characteristic clean flavor and an ethereal bouquet. They are very "dry," namely alcoholic in taste.

The few Irish patent-still distilleries employ similar methods to those used in Scotland.

Kornbranntwein and Schnapps. These two liquors represent the most commonly employed distilled products in Germany. The former is prepared from malt and unmalted cereals, usually rye. Sometimes maize is used and very seldom wheat. The general process of manufacture is similar in principle to that employed for whiskey. Schnapps is usually obtained by diluting rectified alcohol manufactured from potatoes. The potatoes, after cleaning, are placed in large converters, mixed with the necessary quantity of water and heated under a pressure of 30 to 60 pounds, in order to pastify the starch. The mash is then cooled and a small percentage of malt, often green malt, added, so as to invert the pastified starch. After inversion is complete, the fermentation is conducted in the same way as for whiskey. The process of distillation is such that a rectified alcohol results.

Brandy. Under the name of brandy is understood those distilled liquors obtained by the distillation of grape wines, wine-lees or grape pomace. The finest brandy on the market is the so-called cognac. It represents the brandy distilled from the grape wines produced in the department of Charente, France. The town of Cognac is situated here and is the sales-point for the brandy made in this vicinity. France, with its numerous vineyards, is the home of brandy, but considerable quantities are now being prepared in Algiers and in the United States, principally California.

Genuine brandy, being prepared from the finest and purest fermented material, namely, grape wine, is conceded to be the best distilled liquor known. It is characterized by its very fine, smooth alcoholic taste and exquisite flavor or aroma. It possesses a rich golden yellow color and contains from 45 to 55 per cent of alcohol by volume. Different brandies vary in taste and flavor, and the best results are obtained when they are blended together by manufacturers or dealers skilled in this art.

The finest brandies are obtained from a sound, light, white wine that has been stored about one year and is clear in appearance. Inferior wines, such as have soured due to acetic acid development, that possess a mouldy or otherwise foreign taste and odor, or spoiled wines, produce lower grades of brandy. Careful treatment of the affected wine previous to or during the distilling operations often results in brandies of satisfactory quality.

The brandy obtained from wine-lees, namely the yeasty sediment or deposits contained in the fermenters and storage casks, is not quite as fine as that manufactured from grape wine directly. Still, the brandy is of such quality that it can readily be used for blending purposes.

The lowest grades of brandy result from the distillation of the grape pomace, namely, the skins, the pulpy portion of the grapes, and sometimes also the stems. Such brandy has a raw, rank taste and contains much fusel oil, as well as undesirable ethers.

Ordinarily, brandy is distilled from the grape wine shortly after it has fermented and clarified fairly well. The stills used vary from the simplest form to the large continuous apparatus. With simple forms of stills, two distillations are made. The first results in a liquor containing 25 to 30 per cent of alcohol, whereas the second brings the alcohol content up to 65 to 68 per cent by volume. Fractional distillation is often resorted to in order to remove as much of the fusel oil and undesirable ether as possible.

After distillation, the brandy is placed in oak casks, which must be carefully scalded with several changes of boiling water or thoroughly steamed. Usually brandy casks are first filled with white wine, so that an excess of coloring substances or such as could affect the taste of the brandy are removed.

Brandy must be stored four to five years before it acquires the proper taste, flavor and smoothness. Some brands are fifteen to twenty years old before they are marketed, and naturally command a very high price on account of their fine quality. When ready for marketing, the brandy is reduced, blended with other batches and sometimes sweetened as well as colored to suit the requirements of the trade.

Imitations of brandy are numerous; in fact the claim is made that less than one-half of the brandy consumed is genuine. The most common practice of producing cheap brandies is to add diluted rectified grain alcohol to a strongly flavored brandy. The resulting product is then colored and sweetened. Imitation brandies usually receive an addition of œnanthic ether, the so-called brandy or lees oil. This substance is a colorless, oily liquid obtained by the further distillation of the wine-lees after removing the alcohol and water. It possesses a very offensive odor when concentrated, but upon dilution with alcohol, it imparts an agreeable wine odor to it. Much artificially prepared brandy or cognac is made from rectified alcohol, properly diluted, and to which œnanthic ether, an extract obtained from oak wood chips, caramel and cane-sugar syrup is added.

Gin. The word gin is a shortened form of Geneva, which is derived from the old French word "genevre," namely juniper. It is the spirit distilled from a mash prepared from malt together with unmalted cereals, usually rye or barley, sometimes corn, and is flavored by an addition of juniper berries during the rectification of the distillate. Some distillers at the same time also add a very slight amount of oil of turpentine and hops, in order to obtain a more characteristic flavor.

Gin originated in Holland, and even to-day the finest product is produced in Schiedam, Holland, and bears the name of "Schiedam Schnapps." In time it was imitated extensively by English distillers

and such gin is sold under the name of "London Gin." The United States has in late years produced considerable quantities of gin.

Genuine gin is a colorless liquid of delicate flavor and contains about 52 per cent of alcohol by volume. It is extensively imitated, by flavoring diluted alcohol with various essential oils, but such concoctions are decidedly inferior in every respect to the genuine article.

Rum. Among the distilled liquors consumed most commonly, rum has by far the highest alcohol content. A genuine rum never contains less than 70 per cent alcohol by weight (about 78 per cent by volume) and sometimes it is as high as 77 per cent. Rum is manufactured in Jamaica and other West Indies islands, some of the Southern States of the United States, Brazil, Madagascar, East India and some of the Indies islands; in fact in any region where sugar cane is cultivated extensively. The Jamaica rum has the reputation of being the finest in quality.

The materials employed for preparing rum are the molasses, the skimmings (scum or foam) of the sugar kettles, and the juice of the sugar-cane. The higher grades of rum are made from molasses, cane-sugar juice and only very little from the skimmings. Lower grades, often called "nigger rum," are prepared chiefly from the skimmings and other offal products obtained during the boiling and concentrating of the sugar-cane juice when manufacturing sugar. Only little good molasses is employed. Such rum has a pronounced burnt, sourish taste and its flavor is coarse and rank.

The general method of preparing ordinary rum is about as follows:

When boiling the sugar-cane juice, the foam and scum, which is rich in coagulated albuminoids, is skimmed and mixed with some of the fresh juice. About four times the volume of diluted molasses—containing 25 to 30 per cent sugar—is then added. This mixture contains about 12 per cent of fermentable sugar. It is placed in open fermenters, and after three to four days a vigorous alcoholic fermentation sets in. On account of the high temperature, the sugar is readily fermented. Besides alcohol, appreciable amounts of organic acids, chiefly lactic, butyric and acetic acids, are obtained during fermentation.

In order to stimulate the fermentation and increase the yield of alcohol, it is a common practice in the West Indies to use some of the spent liquid from which the alcohol was distilled as yeast food. This liquid is termed "dunder," and contains, besides coagulated albuminoids, a considerable amount of soluble nitrogenous substances and mineral salts, all of which are valuable as yeast nourishment. The employment of this "dunder" for diluting the molasses not only stimulates the fermentation and increases the yield of rum from a certain quantity of the materials, but also has an influence on the taste and flavor of the rum. At the close of a season a number of fermenters are filled with "dunder," which is kept therein until starting the next season.

The freshly distilled rum is a colorless liquid, but soon acquires a pale

yellow to dark amber color from the wooden casks in which it is stored and transported. Sometimes an addition of burnt sugar or caramel is made, if a specially dark color is desired. In order to cover or obscure the peculiar unpleasant taste and odor that is frequently noticeable in batches of rum, an addition of a small amount of certain aromatic leaves, barks or condiments is made at the time of distillation.

The characteristic taste and flavor of the genuine rum cannot be imitated artificially. For this reason imitations can easily be detected by the expert palate. It, however, is a quite common practice to " stretch " rum. This is done by selecting a genuine rum possessing an exceptionally strong bouquet—flavor or aroma being of secondary consideration—and adding from one to four times its volume of rectified grain alcohol that was previously diluted with distilled water until the alcohol content is about the same as that of the rum. This mixture is then stored at about 70° F. for several months to age it, or sometimes the mixture is diluted with more water and distillation resorted to. The resulting liquor is stored in wooden casks until ripe for market. A small amount of so-called " rum-essence " is often added to " stretched " or artificially prepared rum, in order to accentuate the rum taste and flavor.

The distillation and rectification of the alcohol is carried out very carefully. Many operators separate the first one-twelfth volume of the rectified distillate, which has a very strong bouquet, so that it can be used for blending with the later distillations. The first distillate possesses a very " hot " taste and an unpleasant, rank odor, due to the presence of acetic and butyric ethers, volatile acids—chiefly acetic—and certain fatty acids and their ethers.

Slibowitz. This liquor is obtained by fermenting crushed plums and distilling the alcohol obtained by the fermentation. It is practically colorless and possesses a very clean alcoholic taste and odor. Practically no flavor of the plums (prunes) from which it was prepared is noticeable. Slibowitz is made by very many farmers, especially in Hungary and Servia, who use it as a household liquor.

Arrack. The genuine arrack is a type of brandy containing about the same amount of alcohol as found in rum, namely 70 to 80 per cent by volume. It is prepared mostly in Siam, but also in East India, Java and adjacent localities, as well as in Jamaica. The materials employed are either (1) toddy, or palm-wine, (2) rice and toddy, (3) rice and molasses, with or without an addition of toddy.

Toddy, or palm-wine, is obtained by fermenting the sugary juice of the cocoanut palm. This liquid is subjected to distillation in order to obtain the desired alcoholic strength.

When rice is employed, the best grades only are used. The grain is moistened with water until germination sets in. After the greater majority of kernels have started to grow, the rice is crushed between rollers, and hot water gradually added to the starchy mass until the

temperature is about 140° F. The wet starch soon pastifies and is acted upon by the diastase formed during the germination process, and is thus changed to sugar. The fairly clear sugary liquid is strained, cooled to 70 to 75° F., and the desired amount of fermenting toddy added. If molasses or brown sugar is employed, it is generally added at this stage. As soon as the fermentation is over, distillation is started. The stills generally used are very primitive, and in consequence, several repeated distillations, usually three in number, must be resorted to until the desired alcoholic concentration results.

Arrack generally has a yellowish to light-brown color, the substances producing the color being extracted from the wooden casks in which it is kept. It has a peculiar bouquet or flavor which originates from the toddy or palm-wine. If a considerable amount of molasses is used, the flavor or aroma of rum becomes distinctly noticeable, but is not so pronounced that the arrack could be taken for rum.

Vodka. This was the national distilled liquor of Russia. The sale, however, has been prohibited since the start of the war in 1914. The genuine vodka was prepared from rye, employing 15 to 20 per cent of barley malt or green rye malt in order to saccharify the starch. Some of the cheaper grades of vodka were made from potatoes and corn, instead of rye.

Vodka contained from 40 to 60 per cent of alcohol by volume; in fact, it was illegal to sell it if the alcohol was less than 40 per cent. The method of distillation was about the same as that used for patent-still whiskeys.

Liqueurs and Cordials. This name includes a large number of spirituous liquors used as appetizers or after-dinner relishes. The materials employed in their production consist of highly rectified alcohol, cane-sugar, syrup, and flavoring substances obtained from fruits, aromatic herbs and seeds, or perfumes.

The processes of manufacture vary according to the character and quality of the goods. Cheap imitations of well-known high-grade cordials are commonly made. The best liqueurs are obtained by macerating the aromatic flavoring substances in the alcohol and later subjecting the mixture to distillation. The distillate possessing the delicate aroma and flavor is then sweetened with sugar-syrup and colored. The cheaper grades are prepared according to the essence process, which consists in adding the desired essential oils, either of natural or artificial origin, to the alcohol, sweetening and coloring as desired. Another process is termed the infusion process. In this, the fruits, aromatic herbs or seeds or flavoring agents are steeped in the alcohol and sugar. After standing for some time, the liquid portion is strained off and placed on the market.

Liqueurs and cordials vary greatly in taste, flavor, color and alcohol content. In the following are given some that are best known and most commonly consumed:

Chartreuse. Three different types are on the market, namely: green, yellow, and white chartreuse. They have been prepared for centuries by the Carthusian monks, who have zealously guarded their secret of production even to this day. Chartreuse is prepared from a mixture of aromatic herbs and seeds, and possesses a very delicate flavor and taste.

Benedictine. This cordial is altogether different in taste and flavor from chartreuse. The genuine benedictine also is prepared by monks.

Kirschwasser. This liqueur is colorless in appearance and is obtained from cherries. The latter, including the seeds, are crushed and allowed to undergo fermentation. The alcohol is then distilled. The finished Kirschwasser has a pleasant flavor and bouquet, slightly reminding the consumer of ripe cherries.

Maraschino. This is another cherry cordial distilled from the fermented juice of Dalmatian cherries. It is sweetened by an addition of sugar-syrup.

Prune, Peach, Apricot, and Cherry Brandies are prepared from these respective fruits by distillation of the fermented juices. The distillate is either placed on the market as first obtained, or it is sweetened and colored. Sometimes an infusion of the fruit in alcohol also is added to the distillate, or the infusion itself is placed on the market. They all possess the characteristic flavor and aroma of the fruit from which they are obtained.

Absinthe. This cordial formerly was popular in France, but its manufacture and sale are now prohibited. It was prepared by distilling rectified alcohol or brandy in which wormwood, star-anise, green anise seed, fennel, coriander, angelica-root or other aromatics have been macerated for about a week. The resulting liqueur is greenish in color and contains a large amount of volatile oils. On account of the latter absinthe becomes milky when water is added immediately before drinking it. The oil of wormwood has a very powerful effect upon the nervous system, and steady tippling of absinthe causes digestive disorders, induces vivid dreams and hallucinations, and may finally cause paralysis or idiocy.

Anisette. The aromatic seeds used for its preparation are green anise seed, star-anise, and coriander seed. The distillate is sweetened and sometimes also receives an addition of orange-flower water.

Crême de Menthe is a sweetened liqueur, the flavor of which is obtained from fresh mint leaves, usually peppermint. It generally possesses a pronounced green color, although white and red are also on the market.

Crême de Yvette, also called Crême de Violet, has a pronounced odor of violets and also is violet in color, artificially obtained.

Crême de Roses is rose-colored in appearance and is a sweetened liqueur having a pronounced odor of oil of roses.

Crême de Vanilla has a strong vanilla taste and odor.

Crême de Cacao is obtained by making an infusion of cocoa, alcohol and sugar-syrup.

Curaçao. This very fine liqueur is prepared by macerating orange peel, especially from Curaçao oranges, in rectified alcohol for a week or longer. After distillation an addition of sugar-syrup and a coloring substance is made. The finest grades are prepared in Holland.

Aquavit. Although this liqueur is not a cordial in the true sense of the word, a brief description is placed here. It is generally used as an appetizer. Aquavit is manufactured and consumed extensively in the Scandinavian countries, especially Denmark. When the alcohol from grain mashes is rectified, an addition of caraway seeds and orange peel is made in order to impart their flavors to it.

Kümmel is obtained by distilling alcohol in the presence of the herb cumin and caraway seed. An infusion of these in alcohol also is made. The product has a pronounced taste and odor of the caraway seed and is sweetened more or less according to the demands of the trade. It is very popular in Germany.

Industrial Alcohol

Denatured Alcohol. The enormous increase in the demand for ethyl alcohol in various industries where it is needed for manufacturing purposes, caused our government to pass a statute in June, 1906, rescinding the tax that is placed on alcoholic liquors used for drinking purposes. According to this statute, the alcohol thus to be used in the technical arts must be treated as per prescribed formulæ in order to render it unfit for human consumption. The resulting alcohol is commonly known as *denatured alcohol.* The denaturing processes were not intended to render the alcohol poisonous but mainly to give it a disagreeable taste and odor, thereby making it unusable for drinking.

Denaturing Formulæ. The original formulæ for completely denaturing ethyl alcohol called for a mixture as follows:

	Formula No. 1.	Formula No. 2.
Ethyl alcohol (not less than 180 proof)	100 gallons	100 gallons
Wood alcohol	10 "	2 "
Benzine	½ gallon	Pyridin bases ½ gallon

Completely denatured alcohol of this kind was intended mainly for heating, lighting and power purposes. However, the existing prices of hydrocarbon fuels, particularly kerosene and gasolene, are so much lower than the cost at which denatured alcohol can be manufactured, that the use of denatured alcohol for these purposes cannot be considered, even for many years to come.

Since the completely denatured alcohols are unsuited for many industrial purposes, the Commissioner on Internal Revenue was authorized to consider any formula for special denaturation, submitted by manufacturers of the same class of industries. This brought forth numerous

special formulæ and caused a rapid increase in the employment of denatured alcohol. All manufacturers using such special denatured alcohols must give bond that the alcohol will only be employed for the purpose specified and a very careful record of the amounts used must be kept.

The most commonly employed special denatured alcohol is prepared by mixing every 100 gallons of 180 proof ethyl alcohol with 5 gallons of approved wood alcohol. Such is extensively used in the manufacture of various kinds of varnishes and lacquers, photographic dry plates, transparent soaps, solid and powdered medicinal preparations, and many others.

Other special formulæ allow the denaturation of alcohol for the manufacture of sulphuric ether, of explosives, of pyralin, celluloid and similar products, of smoking and chewing tobacco, of imitation leather, and for numerous minor purposes. In such formulæ wood alcohol, benzine, pyridin bases, ether, acetone, nicotine, camphor, castor oil, caustic soda and often certain dye-stuffs are used. Space does not permit a detailed description of the numerous formulæ that our Government has approved and complete information in this respect can be obtained from the Commissioner of U. S. Internal Revenue.

Manufacture. The basic principles of manufacturing denatured alcohol are practically identical to those employed in the preparation of American whiskey of the Bourbon type. Since economy of production is of greatest importance, the percentage of malt used is the minimum, viz., about 10 per cent of the total weight of the material. Indian corn (maize) represents the other 90 per cent. The cheapest grades obtainable are employed and such corn as has been injured by frost, water, heat or mould can readily be used. Any other starchy cereals affected likewise can also be employed for this purpose.

In the distillation of the fermented mash, the alcohol is concentrated to a strength of more than 90 per cent by volume (180 proof-spirit). It is then run into storage tanks or cisterns for denaturation, or the alcohol can be shipped to a different denaturating station. In either event, a strict government control is kept according to the regulations of the Internal Revenue statutes.

Special Materials and Methods. In order to produce industrial alcohol as cheaply as possible, the utilization of certain waste materials rich in carbohydrates has been suggested. Many of these have been given trials on a practical scale, but with the exception of saw-dust and wood refuse, none of the materials has been employed with success. Among the materials tried were saw-dust and wood refuse, cull potatoes, cull fruits, cull sweet potatoes, cannery wastes, molasses, cassava roots, cactus plants and even garbage.

The great problems in using such waste materials are those of obtaining the material, first, at a sufficiently low cost and second, during an ample interim of the year, that the plant can be operated economically. Some

of these materials are obtainable in territory where the cost of collection and of shipment to a centrally located plant would make their cost too high for the production of alcohol at a low figure. The cost of transporting the finished alcohol to the market also is a big factor. Many of them are seasonable and, therefore, are available only for several weeks during each year. This applies particularly to cull potatoes, cull sweet potatoes, cull fruits and cannery wastes.

Cassava roots are not as yet cultivated in large enough quantities to consider them as a source of industrial alcohol. Their growth, furthermore, is limited to the Southern States of this country.

Of late, molasses has increased so much in price that its employment now is out of question.

Cactus plants, especially the fruit, can only be obtained in the Southwestern States and the alcohol obtained therefrom is handicapped by the high freight cost to the market in the Eastern States.

Garbage has been suggested as a source of alcohol and experiments are now being made. Its utilization is feasible only in a most modern garbage reduction plant and where the cost of handling the garbage is very low. Even then it is doubtful whether a sufficient yield of alcohol can be obtained throughout the year to make the operation profitable.

The best solution of the problem of using waste materials of this kind would be small, so-called farmers' distilleries operated at stations where the materials are easily obtainable. Germany thus solved it, but the general system, as applied there, is out of question in our country as long as petroleum fuels and products can be bought at as low a cost as is the case in our country at present.

Alcohol from Wood. The utilization of saw-dust and wood refuse has been given considerable experimentation and there are several plants now in operation where this method of alcohol manufacture is used. The knowedge, both technical and engineering, still is very limited on this subject. It, however, has been determined that a plant of this kind can only be operated at a profit when an ample amount of wood for a long enough time is available, in excess of the fuel needed for furnishing power to the saw mill, and where the cost of handling such wood refuse is very low. The plant is very costly to equip and operate, hence a small distillery is out of the question. The smallest ones now in operation profitably distill not less than 2000 and usually 3000 gallons alcohol daily.

Soft woods yield the most alcohol and hard woods the least. The coniferous woods are generally used and in a well-designed plant about 20 gallons of 190 proof alcohol is obtained per ton (about 1 cord) of the dry wood. The cost of manufacture has been as low as 20 cents per gallon, but 25 to 30 cents is a more average figure. This cost, however, mounts rapidly with the increase in the cost of handling the saw-dust or wood refuse.

The best commercial process consists of hydrolysis of the carbohydrates

by the employment of a small quantity of a mineral acid, usually sulphuric, as a catalyser. The saw-dust, shavings and other small wood refuse are treated with dilute sulphuric acid solution in rotary steel digesters having an acid-proof lining. The mass is subjected to 60 pounds steam pressure for fifteen to twenty minutes, during which part of the wood is changed to fermentable sugars. This digested material is now run into diffusion batteries similar to those used for sugar beets and dye woods. In these the sugar and other water-soluble substances are extracted with hot water. The resulting liquor is then neutralized with lime or limestone. After settling for fifteen to twenty-four hours, the liquid is cooled to 75 to 80° F., set with distillers yeast and the sugar fermented in three to four days. The distilling operations are then carried out as usual.

The question of yeast nutriment is a very important one in the preparation of alcohol from wood. A special yeast mash must be made for each fermentation and the necessary nourishment for the yeast thus supplied. A mash can be made of rye and malt, or malt alone can be used. A cheap material for this purpose is malt culms, because they are very rich in soluble nitrogenous substances of the kind readily assimilated by the yeast. Wheat and rye-bran can also be used with good results.

CHAPTER XLII

TEXTILES

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Definitions. By the term "textiles" is to be understood a class of manufactured articles prepared from "yarns" which are continuous threads composed of fibrous materials. These fibrous materials which form the basis of textile manufactures are of various kinds, including animal, vegetable, and mineral products; for example, wool, cotton, and asbestos. A fiber is really a filament the length of which is comparatively much greater than the diameter, and the latter is of almost microscopic proportions. This allows of several fibers being twisted together by a process known as spinning, so that a continuous and uniform thread is produced. Physically, a textile fiber must possess considerable tensile strength and pliability in order to yield a satisfactory thread. In the case of the shorter fibers, such as cotton and wool, the surface structure also allows of considerable cohesion between the separate fibers when twisted together. Where this cohesive property is lacking, as in silk and some of the cruder vegetable fibers, the strength of the twisted thread depends on the great length of the individual filaments.

Origin. The textile fibers may be classified with respect to their origin in the following manner:

Animal Fibers, consisting (*a*) of the hairy covering of various animals, principally of the sheep, goat, cow, and camel; and (*b*) of the filaments spun by the silk-worm for its cocoon.

Vegetable Fibers, consisting (*a*) of the hairy covering of the seed of the cotton plant; (*b*) of the bast or structural part of the stem of certain plants, such as flax, ramie, jute, and hemp; (*c*) of the structural part of the leaves of such plants as sisal, agave, and certain palms.

Mineral Fibers, of which the only representative is asbestos.

Artificial Fibers, such as artificial silk prepared from solutions of cellulose derivatives, spun glass, and certain metals drawn out to fine filaments. There are also *metallized* yarns, consisting of a core of cotton, linen, or other fiber, coated with a finely divided metal and a suitable agglutinant.

The great bulk of the textile fibers are comprised under the first two

classes, of which the most typical representatives to be considered are: wool, silk, cotton, and linen.

The Animal Fibers. In their chemical nature these fibers are essentially proteid substances of complex organic structure. The basis of wool (and the hair fibers in general) is called *keratin*, a nitrogenous substance containing also sulphur, while that of silk is known as *fibroin*, which is also nitrogenous but does not contain sulphur. In their physical structure the hair fibers are very complex, being composed of minute cells and provided with an external layer or sheath of hard, bone-like tissue or scales. Silk, on the other hand, is a continuous filament without apparent organic structure.

The Vegetable Fibers. The chemical basis of this entire class of fibers is *cellulose*, and as this contains neither nitrogen nor sulphur, it presents a marked chemical difference to the albuminous substance of the animal fibers. In their physical structure the vegetable fibers as a class are comparatively simple; in the case of cotton the fiber consists of a single elongated cell; with the bast and leaf-tissues the commercial fiber consists of a more or less complex aggregate of small cells. Cotton in its natural state, consists of almost pure cellulose, and requires but little purification for use in manufacturing; the other vegetable fibers, however, are associated with a considerable amount of substances other than cellulose and require a rather extensive process of purification for the purpose of isolating the pure cellulose fiber.

Wool. This fiber is the hairy covering (or fleece) of the sheep. It is a growth originating in the skin, springing from a root or hair-follicle. In its physical structure the fiber consists of three portions: (*a*) an inner layer of rounded elliptical cells, called the *medulla*, and often containing pigment matter; (*b*) a surrounding region of elongated spindle-shaped cells, called the *cortical* layer, which forms the major portion of the fiber; and (*c*) an external coating of flattened, hard, horn-like cells, or *epidermal scales*, arranged in such a manner as to overlap like the scales on a fish. This latter peculiarity of structure gives to wool a characteristic microscopic appearance whereby it may be readily distinguished from other fibers (see Fig. 355). The character of fiber produced in the fleece varies largely with the breed and cultivation of the sheep. The merino sheep (now grown principally in Australia) gives a long, fine and wavy fiber, much prized for the manufacture of high-class clothing fabrics. The majority of the wool grown in America (chiefly known by the name of "territory" wool) is of shorter staple and coarser in quality. The arrangement of the epidermal scales also varies considerably with the nature of the fiber. With some wools, these scales

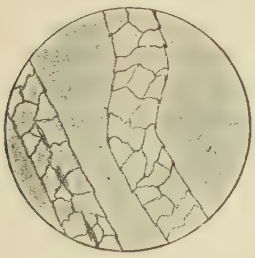

Fig. 355.—Typical Wool Fiber.

are prominent and the free edge projects considerably, giving the fiber a serrated or saw-toothed appearance. Wool of this nature is easily *felted* as the fibers become firmly attached to one another by the interlocking of the projecting scales. In other varieties of wool the external scales lie flat on the surface with very little free edge projecting, hence the surface of these fibers are smooth and do not readily felt together. Another important physical property of wool is its waviness. Some wools (especially the fine merinos) are very wavy, and the waves (or crimps) occur with great regularity throughout the entire length of the fiber; other wools are stiff and straight with little or no waviness, or have very irregular waves. The wavy structure of the fiber enhances its spinning quality, as it allows of a greater coherence among the fibers when they are twisted together. A yarn composed of such fibers also exhibits greater resiliency and sponginess as well as elasticity.

In its *chemical properties* wool is closely allied to gelatin and horn-tissue. It probably consists of a number of chemical bodies, as its proximate chemical composition varies considerably in different samples. Its average composition may be taken as follows:

	Per Cent.
Carbon	50
Hydrogen	7
Oxygen	26–22
Nitrogen	15–17
Sulphur	2–4

From its general chemical reactions the substance of the wool-fiber has been classified as a proteid to which the name *keratin* has been given. This probably contains both amino and acid radicles in its constitution, as it exhibits in a well defined manner both basic and acid properties. The amino-acid existing in wool has received the name *lanuginic acid*, and it may be prepared by dissolving the fiber in barium hydroxide solution, treating with carbon dioxide to precipitate the barium, filtering, and adding lead acetate which precipitates the lead salt of lanuginic acid. The free acid itself may be obtained by decomposing the lead salt with hydrogen sulphide. Lanuginic acid is soluble in water and yields the same reactions with mordants and dyestuffs as wool itself. The wool-fiber is rather sensitive to the action of high temperatures; if exposed to a dry heat of over 100° C. the fiber soon becomes discolored, harsh and brittle. On this account the drying of woolen materials should be carefully conducted to avoid injury. Strong solutions of mineral acids destroy the wool fiber, though dilute solutions are without injury. Sulphuric acid in dilute solution apparently combines in a chemical manner with wool, causing the fiber to become more reactive towards many dyestuffs. Nitric acid gives wool a yellow coloration, supposedly due to the formation of xanthoproteic acid. Nitrous acid apparently causes a diazotization

of the amino radicle in wool, for when so treated the fiber combines with various phenols, with the production of a number of colors. Solutions of alkalies (especially the caustic alkalies) react injuriously with the wool fiber; with even dilute solutions of sodium hydrate wool is rapidly dissolved. This reaction permits of the easy chemical separation of wool from cotton for analytical purposes. With solutions of metallic salts (such as potassium dichromate, alum, ferrous sulphate, etc.) wool reacts in apparently a chemical manner, as it combines with the metallic oxide, and in this condition is capable of uniting with many dyestuffs. This process is termed *mordanting* and the metallic salts employed are known as mordants. When wool is treated with solutions of bleaching powder a product known as *chlorinated* wool is produced; the fiber becomes glossy, harsh, and loses its felting properties. The combination of wool (as well as other textile fibers in general) with various substances, such as metallic oxides, acids, dyestuffs, etc., is probably more of a colloidal than a strictly chemical phenomenon. The substance of the fiber is of such a nature that it is capable of forming colloidal aggregates with various substances, such colloidal aggregates very closely resembling chemical compounds in many of their characteristics.

Scouring of Wool. In its natural state in the fleece wool is contaminated with a number of impurities. These may be classified as follows:

(*a*) *Wool grease*, which occurs in large quantities as an external coating on the fiber; it is a natural exudation of the sheep and serves as a protection to the fiber, preventing it from becoming felted and mechanically injured. It differs from other animal fats in that it does not consist of the glycerides of the fatty acids, and is very difficultly saponifiable with caustic alkalies. Wool grease possesses more the chemical properties of a wax, as it is composed mostly of the higher solid alcohols known as cholesterin and isocholesterin both in the free state and as esters with the fatty acids. Though insoluble in water and not saponifiable by alkalies, cholesterin is easily emulsified, a property on which is based the usual method of wool scouring. Wool grease, however, is easily soluble in naphtha and other volatile solvents.

(*b*) *Suint*, or dried-up perspiration, consisting largely of potash salts of organic acids, and soluble in water.

(*c*) *Miscellaneous dirt*, such as dust, sand, vegetable matters, tar, etc.

Before the wool fiber can be used in manufacturing processes it must first be cleansed from the adhering impurities. This is accomplished by scouring the dirty and greasy wool in a warm soap solution, to which more or less soda ash is added. The temperature of scouring should not be above 140° F., else the fiber will be injured by the action of the alkali. The wool grease is easily emulsified by the alkaline soap solution, whereas the suint is dissolved by the water, the other impurities being removed by the mechanical action of the water. After scouring in the soap solution the wool is thoroughly rinsed in warm water, and finally squeezed and

dried. Another form of wool scouring, known as the *solvent process*, is becoming of great importance in this country. The greasy wool is treated with solvent naphtha in closed kiers, and the resulting solution of wool grease is transferred to stills where the naphtha is recovered and the wool grease is obtained as a by-product. The latter may be further purified and utilized for the preparation of *lanolin* compounds. The degreased wool is next treated with a dilute warm soap solution to remove the suint and dirt. This process leaves the fiber in a much better condition and the recovered grease is of sufficient value to pay for the cost of scouring.

Besides the greasy matters existing on the surface of the wool there is apparently a small amount of oil within the fiber proper and forming an integral part of its constitution. If this oil is removed the fiber becomes harsh and brittle, therefore in scouring of wool either by the soap or the solvent method, it is not desirable to carry the operation too far; there should be about $\frac{1}{2}$ to 1 per cent of natural oil left in the fiber after scouring.

The potash salts existing in wool suint and removed by the scouring are valuable by-products which are capable of recovery. In many European plants these salts, as well as the grease, are recovered and utilized; in this country, however, the wash waters containing the suint are run to waste. The amount of grease and dirt in wool varies greatly with the breed and cultivation of the sheep. The finer stapled wools usually contain the largest proportion of grease. The amount of dirt and vegetable matter will depend largely on the character of the range on which the sheep are grown, a dry sandy soil usually producing a large amount of dust in the wool. The amount of loss caused in scouring wool is known as its *shrinkage* and this amounts to 40 to 70 per cent on the weight of the raw fleece. In America, as a rule, there is no distinction made between the wool grease and the suint, but the total impurities in the fleece are known under the name of *yolk*, as in the usual emulsion process of scouring the entire impurities are removed *in toto* in a single operation.

The recovery of the by-products from waste scouring liquors is gradually being forced upon American manufacturers as an escape from the pollution of streams. Strict laws have been passed in many localities which have necessitated the wool-scourers to erect suitable treating and purifying plants for the removal of the objectionable matters from the waste scouring liquors before such liquors can be emptied into streams.

The scouring of wool is usually conducted by machinery with the object of agitating the fiber in the least possible degree, so as to avoid felting. The machines in general use are long tanks arranged in tandem order. The greasy wool is introduced into the first tank by means of a traveling apron, and is slowly carried through the scouring liquor by moving forks until it is caught up by squeeze rolls and passed into the second tank, where it is carried forward in the same manner through another

soap solution; it is finally carried through a third tank containing fresh warm water for rinsing. The scouring liquor is introduced fresh into the second tank and passes thence into the first tank, so as to have the clean wool coming from the fresh liquor. In some places the spent scouring liquors are worked up to recover the potash salts by simple evaporation and calcination, when from 5 to 10 per cent (on the weight of the raw wool) of potash may be obtained. Again, the spent liquors are sometimes treated with sulphuric acid, in order to decompose the soaps and liberate the fatty matters. The latter, together with the associated wool grease, are settled out on the surface of the liquor from which they are removed. The excess of water is eliminated by hot-pressing in bags. The crude greasy product so obtained is known as *Yorkshire grease*, and has considerable use for dressing leather and as a lubricating grease.

Mechanical Treatment of Wool in Manufacture. After wool has been scoured and dried the next step is to convert it into yarn. In the first place, according to the quality of yarn desired, a close selection of the required grade of wool is made. This is the function of a special branch of the industry known as *wool grading and sorting*. Wool is first graded with reference to the breed of sheep, such as full-blood merino, territory, half-blood, etc. This has reference chiefly to the fineness and length of staple. The long stapled wools are suitable for *combing* and are used for the preparation of *worsted* yarns; the shorter stapled varieties are *carded* and made into *woolen* yarns. In the combing process the shorter fibers (*noils*) are removed from the long ones, leaving the latter to form what is called *tops*, a form of preparation previous to the spinning of the yarn. As the character and quality of the fiber varies considerably at different parts of the same fleece, wool is further graded by *sorting* the fleece into its distinctive portions, such as the loin, back, neck, legs, etc. Usually the fleece is sorted into nine portions. The grading and sorting of the fleece is made previous to scouring.

In the preparation of yarn the first step is combing (for long staples) or carding (short staples). This is for the purpose of removing undesirable matters, such as short fibers, adhering impurities, etc., and also to lay the fibers in a parallel direction and bring the wool into a ribbon-like form so as to permit of the subsequent spinning operations. These latter processes consist in further paralleling the fibers and reducing the thread to the desired size by drawing out and twisting.

Chemical Treatment of Wool in Manufacture. (1) *Bleaching.* The wool fiber in its natural state contains more or less of a yellowish brown pigment. In some cases this pigment becomes greatly accentuated and the fleece may be dark brown or even black in color, but these occasional "black sheep" are of rather rare occurrence. Where it is desirable to have a perfectly white fiber either for purposes of dyeing delicate tints or for white goods, it becomes necessary to bleach the wool. There

are two general methods in use at present for this purpose. In the first, sulphurous acid, SO_2, is used as the active bleaching agent. The well scoured and moistened woolen material is placed in a suitable room and subjected to the prolonged action of fumes of burning sulphur, the time required for complete bleaching being from eight to twenty-four hours, depending on the nature and texture of the material. The process is termed "stoving," from the so-called stove in which the sulphur is burnt. The bleaching room must be so constructed as not to permit of the condensed acid liquor dropping on the goods, which would otherwise be spotted and injured. This process is known as the "gas" or "dry" method of bleaching. After the bleaching is finished the wool is rinsed in a water containing a minute quantity of a blue or bluish-violet coloring matter for the purpose of tinting the white so as to furnish a more pleasing color to the eye. A "wet" process of bleaching may also be employed, the wool being steeped in a dilute solution of sodium bisulphite for some hours, and then passed through a bath of dilute sulphuric acid. The bleached white obtained on wool with sulphurous acid does not appear to be permanent, as prolonged exposure to the air will cause the yellow natural color to return. This has been accounted for by assuming that the sulphurous acid merely reduces the natural pigment to a colorless compound which becomes reoxidized on exposure to the air, resulting in the formation again of the original pigment.

A second process for the bleaching of wool which is coming into considerable favor more especially for fine goods is that which employs sodium peroxide as the bleaching agent. Hydrogen peroxide is also employed to a considerable extent in bleaching. It is probably somewhat more expensive to use than sodium peroxide, but does not offer the disadvantages of the latter in the preparation of the bleaching liquor, which in the case of hydrogen peroxide is also free from sodium sulphate. Sodium peroxide, Na_2O_2, when dissolved in water acidulated with sulphuric acid, yields a solution of sodium sulphate and hydrogen peroxide:

$$Na_2O_2 + H_2SO_4 = Na_2SO_4 + H_2O_2.$$

The hydrogen peroxide in contact with organic substances readily decomposes with liberation of nascent oxygen:

$$H_2O_2 = H_2O + O,$$

and the latter quickly decomposes and destroys the coloring matters in wool. In general outline, then, the process of bleaching wool with sodium peroxide is to prepare a bleaching liquor as follows:

100 gals. of pure water;
5 lbs. 5 ozs. oil of vitriol 168° Tw.);
4 lbs. of sodium peroxide (98 per cent).

The acid is mixed with the water first and then the sodium peroxide is carefully sifted in. These proportions should leave the bath in a slightly acid condition; this is essential, as otherwise caustic soda would be present from the incomplete neutralization of the sodium peroxide, and small traces of that alkali in the bath would be very injurious to the fiber. Before using the bath for bleaching it is neutralized by the addition of the requisite amount of sodium silicate, ammonia, or borax. This is necessary because the bleaching effect is much enhanced in a slightly alkaline solution. The woolen material (which has previously been well scoured) is then entered and manipulated sufficiently to thoroughly saturate the fibers, after which the wool is left in the liquor for ten to twenty hours when the bleaching should be complete. All the materials employed in the preparation of the sodium peroxide bath must be very free from iron, otherwise the bleaching will be imperfect. In preparing the bleaching solution from hydrogen peroxide the procedure is much more simple. Hydrogen peroxide comes into trade in the form of a 3-per-cent solution contained in carboys This solution is simply diluted with water so as to furnish a $\frac{1}{2}$-per-cent solution of hydrogen peroxide, that is to say 1 gallon of hydrogen peroxide liquor is mixed with 5 gallons of water. Then sufficient sodium silicate or ammonia is added to make the bath distinctly alkaline in reaction. In some cases a 1-per-cent solution of hydrogen peroxide is used for bleaching. The bleaching vat should be of wood and all necessary pipes should be of lead. The temperature of the bath should be maintained at about 100° F. during the entire time of bleaching. The white color obtained by this method of bleaching is a permanent one, as the pigment matter in the fiber is completely destroyed. It also leaves the fiber free from any deleterious substance, hence is to be preferred to the sulphur method, which nearly always leaves a residue of sulphurous acid (or its compounds), and this acts injuriously on many coloring matters which may be used in the after-dyeing of the bleached wool. Unfortunately the cost of the peroxide method is still too high to permit of its general adoption for all cases of wool bleaching.

Wool may also be bleached by treatment with a cold dilute solution of potassium permanganate. The pigment in the fiber is rapidly destroyed by the strong oxidizing action of this chemical, but the resulting decomposition of the permanganate precipitates a brown hydroxide of manganese on the fiber, hence it is necessary to pass the wool through a second bath containing a weak solution of sodium bisulphite which removes completely the deposit of manganese compound and leaves the wool perfectly white. Oxalic acid will also have the same discharging effect on the brown oxide of manganese, and is sometimes employed in place of sodium bisulphite. This method gives a very rapid process for bleaching, but it is rather costly. Wool, however, which had been bleached with sulphurous acid, is often treated with a very dilute solution of potassium

permanganate, to insure the complete removal of all residual sulphurous acid compounds from the fiber. Wool may be bleached in almost any stage of its manufacture; as loose stock, tops, yarn, or cloth.

Carbonizing. Woolen material is often contaminated with small quantities of vegetable fiber, and as the latter does not become dyed in the same manner as the wool, it shows itself in the form of specks. To purify the cloth (or other form of manufactured wool) from these specks, the vegetable fiber is destroyed by treatment with a dilute solution of sulphuric acid (6° Tw.) and subsequently drying at 180 to 190° F. This "carbonizes" the vegetable matter, or reduces it to a brittle friable substance, which is easily removed by beating and washing the woolen material. Dilute solutions of aluminium chloride (10 to 12° Tw.) may also be used for the same purpose, as on drying this salt is decomposed with liberation of hydrochloric acid. The latter method is used chiefly where dyed materials are to be treated, as the colors are less affected than when sulphuric acid is employed. The process of carbonizing is also largely employed for the purpose of recovering the pure wool fiber from rags containing mixtures of wool and cotton yarns. The resulting product is known as *shoddy* or *mungo* and has a large use in the woolen industry.

Crabbing. This is a process for removing the crinkle or curl from cloth or yarn caused by the uneven shrinkage or curl of the fiber. It depends on the fact that when the wool fiber is subjected to a moist heat it becomes plastic and can easily be straightened out by stretching. If the fiber is then cooled in the stretched condition it will preserve its straight form permanently. Tightly twisted worsted yarns are very liable to curl up. This may be remedied by treating the stretched yarn with steam or boiling water, and then allowing to cool while still in the stretched condition. Cloth containing tightly twisted-in curled yarns or containing a mixture of woolen and cotton yarns will crinkle up or pucker owing to uneven contraction of the yarns in finishing. This may be removed by passing the stretched cloth alternately through boiling water and cold water, or better yet by tightly winding the cloth on a perforated cylinder and blowing steam through it, then subsequently cooling. The crabbing process in the case of cloth is also known as *decatizing*, and is extensively used for the production of a high-lustre finish on such fabrics as broadcloth, etc.

Fulling. This process is also known as "milling." It is a felting action produced on the wool fibers in a fabric by the combined action of soap and friction. The projecting scales on the individual fibers become interlocked so that the fibers firmly adhere together. This action causes the cloth to shrink considerably and at the same time become more continuous and homogeneous in its structure. If the operation of fulling is carried on to its full extent a *felt* is made of the cloth. Acid solutions, and even boiling water, combined with friction will also produce fulling. In this manner hat felts are produced.

The Minor Animal Fibers. In addition to wool there are also a number of other animal hair fibers employed to a limited extent in the manufacture of textiles. The woolly fibers of different species of goats are utilized in much the same manner as wool itself. *Mohair* is obtained from the Angora goat. The fiber is long, fine, smooth and highly lustrous. It is largely used for the manufacture of plushes, braids, and linings. *Cashmere, alpaca,* and *llama* are also fibers from species of goats. All of these animal hair fibers are similar in chemical composition to wool; their physical structure is also very similar.

Silk. Though silk is also an animal fiber and somewhat similar to wool in its general chemical properties, it differs very widely from that fiber in its physical structure and properties. The silk fiber is a fine continuous filament spun by the silkworm in the preparation of its cocoon. The fiber as spun by the caterpillar consists of two filaments composed of a proteoid substance called *fibroin* and surrounded and cemented together by a glue-like substance known as *sericin* or silk-gum. The silkworms are cultivated principally in China, Japan, Italy, and southern France. Their chief food consists of the leaves of the mulberry tree, hence the caterpillar is known as the mulberry silkworm, or *Bombyx mori*. The cocoons are irregularly ovoid in shape and the length of the fiber in them varies from 350 to 1200 meters, while its average diameter is 0.018 mm. The silk fiber as used in manufacturing is prepared by *reeling* from the cocoons. When the cocoons have been completed by the silkworm they are collected and heated in an oven to a temperature of 60 to 70° C. for the purpose of killing the pupa within. Or, the cocoons may be steamed for a few minutes which serves the same purpose. The cocoons are then sorted for size, color, damage, etc., so as to obtain a uniform product. They are then placed in a basin of warm water which softens the enveloping silk-glue and permits of the unwinding of the cocoon thread. The fibers from several cocoons are brought together and passed over a suitable reel where they are slightly twisted together to form a thread of sufficient size for weaving. The adhering silk-glue becomes hardened again, so that the thread presents a uniform appearance. This silk is reeled into skeins of convenient size and comes into trade as *raw silk*. Owing to the presence of the silk-glue it is stiff and wiry and translucent in appearance. Some varieties are of a creamy white color, while others are quite yellow. This yellow color, however, exists only in the silk-glue and is removed along with the latter. *Organzine* silk is prepared from the highest grade of cocoons, and by reason of its superior strength it is employed for warps. *Tram* silk is weaker and is used for filling. In the reeling of silk a large amount of waste is produced. This is scoured in a solution of soap and soda in order to remove the silk-glue, and the residual fiber is then carded and combed and is used for the preparation of *spun silk*.

An inferior grade of waste silk from imperfect and damaged cocoons is

known as *silk noils*. This is used for making low-grade coarse silk yarns, for blankets, rugs, etc.

Boiling-off of Silk. The reeled silk as it appears in trade consists of 70 to 75 per cent of fibroin or fiber proper and 30 to 25 per cent of sericin or silk-glue. For purposes of manufacture it is necessary to remove more or less of the silk-glue. For this purpose the skeins of raw silk are treated near the boil in a strong solution of soap (about 1 lb. per gallon). The soap must be of the best quality and free from uncombined alkali as the quality of the silk is greatly deteriorated by the presence of even a trace of the latter substance. When all of the silk-glue is to be removed it will be necessary to boil the silk for several hours in two or more soap solutions. It is best to maintain the temperature just under the boiling-point to prevent the tangling of the fine silk fibers. The soap solutions are used continuously for the boiling-out of several batches of silk until they became heavily charged with dissolved silk-glue. The spent soap solution is known as *boiled-off liquor* and is largely used in the preparation of the dye-bath for silk. Raw silk will shrink about 25 per cent in weight when boiled-off. More frequently it is not desirable to remove all of the silk glue, but only sufficient to allow of the fiber being subsequently dyed, bleached, or otherwise processed. When 10 to 15 per cent in weight is lost by scouring the process is termed *soupling*. When the boiling-off removes only 2 to 5 per cent in weight the product is known as *écru* silk.

The Chemical Nature and Properties of Silk. Though silk is somewhat similar to wool in its general chemical properties it differs from that fiber in that it does not contain any sulphur in its composition. Silk is readily attacked by alkalies, especially in hot solutions, though it is more resistant in this respect than wool. The caustic alkalies slowly dissolve the silk fiber on boiling, whereas the alkaline carbonates are much less destructive, but even these reagents slowly attack the fiber. Concentrated hydrochloric acid rapidly dissolves silk even when cold. Dilute mineral acids are absorbed by the fiber in the same manner as with wool, and may be employed in the dyeing of silk. Dilute solutions of nitric acid are employed for the bleaching of silk. The effect of dilute acid solutions on silk, especially when dried into the fiber, is to increase somewhat the luster and to give the silk what is called *scroop*—that is, it produces a crackling rustling sound when rubbed or compressed. This property is best imparted by steeping the silk in a bath of dilute acetic, tartaric, or formic acid, squeezing and drying without washing. Hard water (containing lime) should be avoided when dyeing or bleaching silk, as it affects the luster of the fiber, and makes it brittle. Chlorine, and oxidizing agents in general, rapidly destroy the silk fiber, except when employed in very dilute solutions. Silk is capable of absorbing metallic salts from solutions and fixing the oxide of the metal in the fiber. On this action is based the process of mordanting and weighting silk. Tannic

acid is also absorbed by the fiber in large proportions. For purposes of mordanting, silk is steeped successively in baths containing tannic acid (cutch, myrabolams, etc.) and an iron salt (such as pyrolignite of iron or "nitrate of iron," which is really a ferric sulphate). By repeating these treatments a number of times the silk may be *weighted* to a considerable extent, frequently as much as 100 per cent. This method of weighting is principally used as a preparation for the black dyeing of silk. Where colors are to be dyed, the silk is usually weighted with tin salts, the fiber being treated with successive baths of stannic chloride, sodium phosphate, and sodium silicate. A high degree of weighting can also be obtained in this manner.

The proximate composition of the fibroin of silk is as follows:

Carbon	48.3%
Hydrogen	6.5
Oxygen	26.0
Nitrogen	19.2
	100.0

These figures refer to the purified fibroin free from all silk-glue or other contaminating substances. As different samples of silk give slightly different results on analysis, it is probable that the silk fiber is a composite substance and not an individual chemical body. The sericin, or silk-glue, has the following composition:

Carbon	48.8%
Hydrogen	6.2
Oxygen	26.0
Nitrogen	19.0
	100.0

Thus it will be seen that the sericin is very close to the fibroin in its chemical composition. The former, however, is slowly soluble in warm water and readily soluble in soap and alkaline solutions, whereas the fibroin is not.

Physical Properties of Silk. When examined under the microscope the raw silk fiber is found to consist of two more or less parallel filaments rather firmly cemented together by an envelope of silk-glue. Due to the process of reeling from the cocoon, irregular shreds and lumps of silk-glue will also be noticed adhering to the fibers (see Fig. 356). This microscopic appearance of silk is quite characteristic, and serves to distinguish it from other fibers. No indication of internal structure can be noticed in the case of the purified fiber: it merely resembles a translucent glass rod, smooth and regularly cylindrical.

As already noted raw silk is harsh and wiry in handle and rather lusterless in appearance. This is due to the envelope of silk-glue surrounding the fiber. When this is removed the fiber proper appears as a white, soft, and highly lustrous fiber. It possesses a remarkably high tensile strength and great elasticity. Silk is also a good nonconductor of heat and electricity.

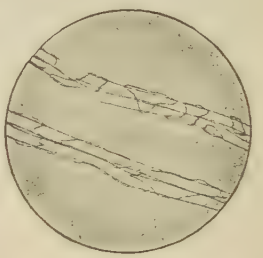

Fig. 356.—Silk Fiber. Cocoon threads showing double filaments and adhering silk glue.

Wild Silks. Besides the ordinary variety of cultivated or mulberry silkworm, there are a number of other silkworms which grow wild, yet furnish cocoons which yield a considerable amount of commercial silk. This fiber is generally known under the name of *tussah* or *tussur* silk. It is of a brownish color, and is harsher and coarser than mulberry silk. It is also much harder to boil off and to bleach and dye. It is largely used for the manufacture of plush fabrics, imitation sealskin, etc., and also for a dress material known as "pongee" or tussur silk. Wild silk can readily be distinguished under the microscope, as the fibers are broad, and the cross-section is flat and triangular. Longitudinal striations are also very distinct, as well as peculiar oblique cross-markings caused by the overlapping of the fibers on one another in the cocoon before the fibroin has become hardened.

Bleaching of Silk. For most purposes silk is sufficiently white without bleaching, but where very delicate tints are to be dyed or where a very pure white fabric is desired, it is necessary to bleach out the slight tint of yellow to be noticed in natural silk. Silk may be bleached in much the same manner as wool, using either the sulphurous acid or the sodium peroxide process. The latter method is to be preferred in the case of silk, as it furnishes a nicer product, and the bleach is not liable to become yellow again on exposure. The extra cost of this process is not a drawback when employed for silk as when used for wool, as the comparative value of the fiber itself is far greater. Silk was formerly also bleached by treatment with dilute cold solutions of *aqua regia*, but as this process was very liable to cause injury to the fiber unless very skilfully conducted, it is not now employed to any extent.

Cotton. The cotton fiber consists of the hairy covering of the seeds of the cotton plant, or *gossypium*. There are a large number of species and varieties of the cotton plant, the principal of which are the following:

Gossypium barbadense, producing silky and long-stapled fibers, the principal representatives of which are the *Sea-Island* cotton of the Southern Gulf States, Egyptian cotton, and Peruvian.

Gossypium hirsutum, which includes most of the cotton grown in the United States and forms the great bulk of the cotton used in trade. It is known as *upland*, *peeler*, or simply *American* cotton.

Gossypium herbaceum, including the majority of the cotton grown in India and China, as well as the small amount which is grown in Italy. The fiber is very short and inferior to that of the two preceding varieties.

Gossypium arboreum, comprises most of the cotton in Asia Minor. This variety grows to the dimensions of a tree in contradistinction to the other varieties which are all shrubs. The fiber is of poor quality, being short and coarse and of a greenish color.

The seed hairs of cotton are developed in a boll as the fruit of the plant ripens, and when maturity is reached the boll bursts open liberating a fluffy white mass of fibers. These fibers are firmly attached to the surface of the seed, and after the cotton is picked from the plant the fiber must be detached and separated from the seed by a process known as *ginning*. The ginned fiber is then baled and distributed to the spinning mills. The seed which is left now forms a valuable by-product of the industry. It is first subjected to a second process of ginning for the purpose of removing the short undergrowth of fibers known as neps or linters, and these are used in the manufacture of wadding and cotton batting and also for the preparation of pyroxylin and gun-cotton. The cleaned seeds are then hulled, and from the separated meal the oil is extracted by cold and hot pressing and steaming. The cottonseed oil so obtained is a very valuable product, the finer qualities being used for salad oils and other culinary purposes, while the lower grades are extensively used for soap-making. The residual meal is used as a cattle-food, and other residues find use as fertilizers.

Before being utilized by the spinner, cotton is graded with respect to length and fineness of staple, color, cleanliness, and other qualities. The value of the fiber is determined by this classification, the basis being what is known as "middling" cotton, the various grades going up and down from this standard.

Physical Properties of Cotton. The cotton fiber consists of a single cell, narrow and elongated, with one end fastened to the seed and the other tapering to a point. During its growth it is tubular, being cylindrical in shape with comparatively thin cell-walls and an inner canal or *lumen*. When the fiber ripens, the sap in the inner canal is absorbed, the cell-walls collapse, leaving a flat ribbon-like fiber with thickened edges. By the unequal drying of the fiber it becomes twisted spirally on its axis. These spiral twists give to cotton its good spinning qualities, for when twisted together the fibers cohere to one another to give a strong thread. The different varieties of cotton exhibit considerable variation in length and fineness of staple. Sea-Island cotton has an average length of about 1.6 ins. and a diameter of 0.00065 in. Ordinary American cotton varies from 1.5 to 0.75 in. in length and has a diameter of about 0.00075 in. Egyptian cotton has a staple slightly shorter than Sea-Island, and of about the same fineness. The South-American and Indian

cottons are comparatively short and coarse, averaging about 1 in. in length and 0.00085 in. in diameter. The physical character of the fiber in any lot of cotton is very variable, hence in manufacturing it is necessary to separate the short fibers from the long by a process of combing or carding; the longer fibers being used for the better grade of yarns and the shorter fibers for the coarser yarns. The degree of ripeness of the fiber also determines its general character; unripe fibers have a very attenuated cell-wall and consequently are weak and brittle. The mature fiber has a thicker wall and a much greater strength. Sea-Island, American, and Indian cottons contain very little natural pigment, being quite white in appearance; the chief varieties of Egyptian cottons, however, are rather highly tinged with a brownish color which is quite distinctive. The microscopic appearance of cotton is quite characteristic and serves to distinguish it readily from other fibers either of animal or vegetable origin (see Fig. 357). The flat, twisted, ribbon-like appearance is very noticeable.

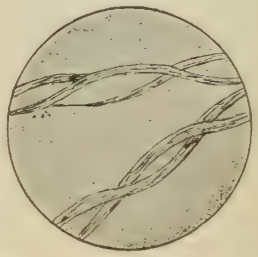

FIG. 357.—The Cotton Fiber.

Chemical Properties of Cotton. In common with all other vegetable fibers, cotton is composed essentially of *cellulose;* in fact, the purified fiber may be considered as almost chemically pure cellulose. In its natural condition, however, there is associated with the cellulose a small amount of waxy and oily matter, which evidently acts as a protective layer on the surface of the fiber. The composition of the natural fiber is about as follows:

Cellulose ($C_6H_{10}O_5$)	91.00
Waxy and fatty matters	0.50–0.40
Nitrogenous matter	0.70–0.50
Moisture	7.00–7.50
Ash (mineral matter)	0.80–1.20

The presence of the waxy coating on the raw fiber causes it to be water-repellent, hence difficult to impregnate with solutions. On this account, cotton material must be boiled out for dyeing or bleaching; that is to say, the wax must be removed by boiling in a dilute solution of caustic soda, soda ash, soap, or other alkaline substance. Certain oils, such as Turkey-red oil (sulphonated castor oil) also have the property of rapidly removing the cotton-wax. The presence of this wax, however, aids considerably in the spinning of cotton as it makes the fiber more plastic and coherent. On this account dyed and bleached cotton does not spin as satisfactorily as raw cotton. In its general chemical reactions cotton behaves in the same manner as ordinary cellulose. The fiber becomes rapidly disintegrated by the action of mineral acids, even in comparatively dilute solu-

tions, and this is especially true when any of the acid liquor is allowed to dry into the fiber. Hence, in all operations of dyeing, bleaching, etc., where cotton may come into contact with acid solutions. it is very necessary to thoroughly remove the acid by continued washing or to neutralize it by a treatment with an alkaline solution. The organic acids which are volatile (such as acetic and formic) do not have much effect on cotton, and in consequence are generally employed in operations where the use of an acid is required for this fiber. The non-volatile organic acids (such as tartaric and oxalic) when allowed to dry and crystallize in the fiber affect it injuriously. Concentrated sulphuric acid converts cotton into a product known as amyloid or vegetable parchment. Concentrated nitric acid reacts with cotton to form a series of nitrated celluloses known as *pyroxylins*, which are utilized for a variety of commercial purposes. Among these derivatives may be mentioned *guncotton*, which forms the basis of numerous high explosives; *collodion*, which is a solution of pyroxylin in a mixture of ether and alcohol, and which is extensively used in surgery and photography as well as for the production of artificial silk filaments; *celluloid*, obtained by dissolving nitrated cellulose in molten camphor. The decomposition product of cotton with dilute mineral acids is known as *hydrocellulose* or *oxycellulose;* the acid evidently produces a hydration of the cellulose molecule with a consequent breaking down of its organic structure. Tannic acid reacts in a special manner with cotton; solutions of this acid do not produce a weakening effect on the fiber, though the acid is absorbed by the cellulose apparently with some degree of chemical combination. This reaction is the basis of mordanting cotton for the dyeing of basic colors. Tungstic acid exhibits a similar reactivity toward cotton.

Dilute solutions of alkalies, under ordinary conditions, have no harmful effect on cotton even at a boiling temperature, consequently such solutions are universally employed for the cleansing or scouring of cotton and cotton goods in general. A concentrated solution (40 to 60° Tw.) of caustic soda has a remarkable effect on cotton. The cellulose apparently combines with the alkali, the fiber swells up, losing its flat ribbon-like appearance to become tubular and semi-transparent. This process is the basis of the modern method of *mercerizing*. The product of combination between cotton and caustic soda is known as *alkali-cellulose*; it is easily decomposed by treatment with water, giving a product known as *hydrated cellulose*, which is the final form of mercerized cotton. Alkali-cellulose is soluble in carbon disulphide, forming a thick viscous solution of cellulose xanthate known as *viscose*. This latter substance has various industrial applications, such as the preparation of artificial silk, paper sizing, transparent films, etc. Cotton is unlike wool in its reactivity toward solutions of metallic salts; whereas the latter readily absorbs and combines with various metallic salts, cotton is especially inert in this respect. On this account cotton cannot be mordanted in the same manner

as wool. With oxidizing agents such as chlorine potassium permanganate, and chromic acid, cotton is readily converted into *oxycellulose*, a brittle friable substance. On this account care must be exercised in the bleaching of cotton with chloride of lime to prevent the too vigorous action of chlorine on the fiber. Cotton can withstand a much higher temperature than wool without decomposition, though when subjected to a heat of over 160° C. the fiber suffers structural decomposition.

Bleaching of Cotton. On account of the nature and the small amount of impurities present in the raw fiber, cotton does not require a previous scouring operation to fit it for manufacturing processes. Previous to dyeing, however, cotton must be scoured or "wet-out" for the purpose of removing the waxy coating so that the fiber may be able to easily absorb the dye solutions. This is accomplished by boiling the material in a weak solution of caustic soda, soda ash, soap, or Turkey-red oil. The use of enzymic bodies like diastase is also recommended for this purpose as these readily solubilize the pictin and waxy matters on the fiber. When cotton is to be bleached, not only the waxy coating must be removed to permit of wetting-out, but as far as possible all of the impurities on the fiber must be removed. This process is termed "boiling-out," which is usually accomplished in the circulating kier, Fig. 358. Cotton may be bleached in any form of its manufacture. It is occasionally bleached in the loose state before spinning, in which case special machines are employed which allow of the bleaching liquors being circulated through the cotton without motion of the fibers, so as to avoid matting and injury to the latter. Instead of boiling-out with alkalies, cold water is circulated through the cotton under pressure, which has the effect of removing the majority of impurities on the fiber without materially dissolving the cotton-wax. Cold bleaching liquors, wash waters, acid solutions, etc., are then circulated in the same manner. The result is a bleached cotton which still retains considerable wax, so the spinning qualities of the fiber are not materially injured. If loose cotton is thoroughly boiled-out and bleached in the usual manner, the fiber will be harsh and will not spin well. Cotton waste and linters are also bleached largely in the loose state for the preparation of absorbent cotton. In this case, as it is not necessary to retain the spinning qualities but to make the fiber as pure and as absorbent as possible, a very thorough boiling out with caustic soda is given before the bleaching.

Cotton yarn is very extensively bleached, both for white goods and as a preparation for the dyeing of delicate shades. The yarn in the form of skeins is usually bundled together and systematically packed into a closed iron kier. The latter is so constructed as to permit of the circulation of a boiling alkaline solution under pressure (5 to 10 lbs). through the yarn. The boiling-out solution usually consists of a mixture of caustic soda and soda ash. Sometimes so-called "bleaching assistants" are used; these mostly consist of soda ash mixed with a small amount

of caustic soda and sodium silicate. For the proper boiling-out of the yarn it is essential that the liquor be circulated evenly and thoroughly through the goods. The amount of alkali employed is about 2 to 3 per cent on the weight of the yarn, and the time of boiling varies from one and one-half to eight hours, depending on the kier employed and the pressure. Overboiling by the use of too much alkali or too prolonged a treatment will render the yarn harsh and brittle and also cause yellow stains. The presence of air in contact with the superheated yarn in the kier will also cause oxidation resulting in weak places and stains. After the yarn has been boiled-out it is washed with fresh water, usually in the same kier, and then worked in a cold dilute solution of chloride of lime (bleaching powder or chemic) at $1\frac{1}{2}$ to 2° Tw. For this purpose the yarn is either hung in sticks and steeped in the chemic solution in ordinary dye-house vats, or better yet it is placed in a machine (Fig. 359) where it may be automatically worked in the solution. The treatment with the bleaching liquor usually lasts from three-quarters to one hour. The yarn is then rinsed in fresh water and next *soured* by treatment with a cold solution of sulphuric acid at about 1° Tw.; hydrochloric acid may also be used. The acid treatment is for the purpose of decomposing the lime compounds retained by the fiber. Where sulphuric acid is used calcium sulphate is formed, which is easily removed in the subsequent washing. Hypochlorous acid and free chlorine are also liberated in the fiber which furthers the first bleaching action of the chloride of lime solution. This is evidenced by the fact that the cotton becomes much whiter in appearance when treated with the acid; also the presence of chlorine is to be noted from its pungent odor. When hydrochloric acid is used for the souring, the very soluble calcium chloride is formed which is very easily removed from the cotton by washing; otherwise the action of the acid is the same. After the acid treatment, it is necessary to

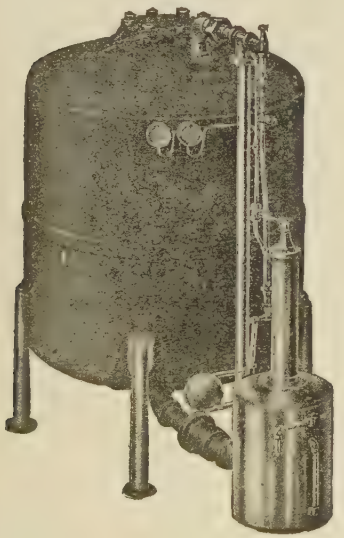

Fig. 358.—Circulating kier for boiling-out of cotton. Jefferson type.

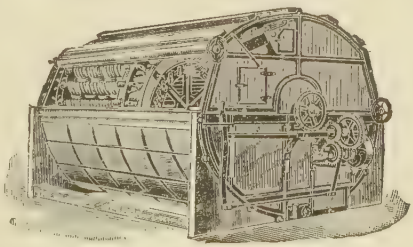

Fig. 359.—Machine for bleaching cotton skein yarns.

give the cotton a very thorough washing to remove as completely as possible the residual acid liquor and the lime compounds from the fiber. If this is not done the yarn will be harsh and tender after drying. The washing should be continued until the yarn shows no indication of acid when tested with blue litmus paper. Finally the yarn is treated in a dilute lukewarm solution of soap or other suitable finishing compound, and if a bluish tone of white is desirable a suitable bluish-violet coloring matter is added for tinting purposes. The bleaching process with chloride of lime is an oxidation process; the chlorine itself, which is the active constituent of the bleaching powder, does not directly destroy the coloring-matter in the fiber. In the presence of water, however, the chlorine liberated in a nascent condition from the chloride of lime reacts with the formation of oxygen, and it is the latter which acts on the coloring matter.

Skein yarn may also be bleached by being linked together in the form of a long chain and run continuously through machines provided with squeeze rollers. Yarn in the form of prepared warps may also be bleached in a similar manner. There are also special machines for the bleaching of cotton slubbing and yarn in the form of cops and tubes, the yarn or slubbing being wound on perforated tubes and so arranged on the machine that the bleaching liquors are forced through the cotton either by means of vacuum suction or pumps.

Cloth bleaching is the principal method, however, for the bleaching of cotton. There are several methods of carrying out this form of bleaching depending on the ultimate use to which the goods are to be put. When the cloth is destined to be sold as white muslin the process is known as the *market bleach;* when the cloth is subsequently to be dyed with alizarin colors (especially red), a so-called *Turkey-red* or *bottom bleach* is given; whereas cloth intended for printing is given the *madder bleach.* These names are quite old in their application and are falling into disuse as characteristic terms. In bleaching for white goods for the market it is desirable to obtain a clear white color with a bluish tint, and the appearance of the goods also depends to a considerable degree on the finishing processes given the cloth after bleaching. The Turkey-red bleach is only for the purpose of providing a white bottom for dyed colors so that the latter will appear bright and clear. The bleaching required of print cloth is by far the most complete and thorough, as it is necessary to remove all impurities from the goods so as to leave the cotton not only white in color but also in the form of chemically pure cellulose so that the printing colors may be properly applied. A general outline of the various processes in this method of bleaching is as follows:

Marking. The cotton pieces as they come from the loom are stitched together and marked with a special ink capable of resisting the bleaching operations so they may be subsequently identified.

Singeing. The cloth is passed rapidly through a series of gas jets so

as to burn off the loose fibers and lint from the surface. The singeing may be done on one side only or on both sides as required. Instead of being passed through gas jets the cloth may be passed over curved copper plates heated to redness, or over a heated revolving copper roller. Singed cloth gives a clear even surface so that fine and delicate patterns may be sharply and clearly printed.

Gray Wash. This is a preliminary wetting out in water and has for its purpose the removal of much of the external dirt as well as the softening and removal of much of the sizing used on the warp yarns in weaving the cloth. This operation is frequently omitted.

Boiling-out. This is a similar operation to the boiling-out of cotton yarn. It is usually conducted in large closed iron kiers, Fig. 358, provided with a suitable mechanism for the circulation of the liquor through the goods. The boiling is usually conducted under pressure (from 10 to 80 lbs.) for from six to eight hours. It was formerly the custom to give a first boiling with milk of lime (lime boil). The goods were passed through a solution of milk of lime and without squeezing were packed into the kier; sufficient water was next introduced and the kier boiled with superheated steam. The lime boil was considered necessary to decompose the fatty matters in the cotton with the formation of a lime soap, and also to convert the starch (or other dressing materials on the cloth) into a soluble form. Of late years, however, the lime boil is being dispensed with as a preliminary operation, and the boiling out is done in one operation with caustic soda. When the lime boil is used it is necessary to give a thorough washing to the goods and then to pass them through a weak bath of sulphuric acid (1° Tw.) known as the *gray sour.* This is for the purpose of dissolving out the lime compound in the fiber as well as any iron stains which may have formed in the kier. After the acid treatment another thorough washing process is required. After the gray sour the goods are given a second boiling in the kier with caustic soda; generally mixtures of caustic soda, soda ash, and rosin soap are employed, and from two to three boilings are given. These boilings remove all of the waxy and fatty matters and most of the pectin compounds in the fiber. The use of rosin was once considered essential to the perfect scouring of cotton for purposes of print-cloth. At the present time, however, the tendency is to omit the rosin boil; in fact, the boiling-out is reduced to the single operation of treating in the kier with caustic soda solution.

Washing. After the boiling-out, in whatever manner it may be conducted, the goods are very thoroughly washed in order to remove as far as possible all of the decomposed impurities and residual alkali. The washing is conducted in special forms of washing machines and well flushed with fresh water.

Chemicking. This is the general term given to the treatment with the solution of bleaching powder. The strength of the solution employed is usually $1\frac{1}{2}$ to 2° Tw., and the liquor should be clear and free from

undissolved particles or sediment. The damp cloth is saturated with this chemic solution, passed through squeeze rolls, and then piled up and left exposed to the air for some hours. This allows the carbonic acid of the air to react with the bleach liquor with the formation of free hypochlorous acid, which destroys the coloring matter present through its strong oxidizing action. Care must be had not to allow the oxidizing action to proceed too far or the cotton fiber itself will be attacked and weakened by the formation of oxycellulose. In some methods of bleaching, instead of exposing the cloth to the action of the air, it is steeped in the solution of bleaching powder for some hours, or the cloth is packed in suitable kiers and the chemic solution is circulated through it by means of pumps.

Souring. After treatment with the chemic solution the cloth contains a considerable amount of lime compounds and undecomposed chlorine derivatives. The souring, or treatment with a dilute solution of sulphuric acid 1° Tw., is for the purpose of removing or decomposing these compounds. The cotton also becomes much whiter in color after the treatment with acid, hence this process is known as the *white sour* (in contradistinction to the gray sour when a lime boil is used). Instead of using sulphuric acid for souring, hydrochloric acid is sometimes employed, as the lime salt with this latter acid is much more soluble; hence much easier to remove from the fiber. After souring a very thorough washing must be given the cloth in order to remove all salts and acid residue.

Finishing. The final operation in bleaching cotton cloth is to give it a finish suitable to the use for which it may be intended. In the case of a market bleach, the cloth must be tinted to a proper tone of bluish white and also be starched and calendered to give it a smooth and polished surface. Cloth intended for dyeing, of course, is not tinted, and receives its special finish after it is dyed. Print-cloth is also not tinted, and it is finished in the printing operation.

Modern practice tends to simplify the operations of bleaching; instead of first boiling with lime, then giving a gray sour and a second boiling with soda ash and resin soap, a single boil with caustic soda is given in a pressure kier for ten to twelve hours.

Of late years a number of bleaching processes have been brought forward with the object of making the process shorter and more automatic. Special forms of kiers have been devised where the cloth is treated to all the operations with a minimum degree of handling. One such method which is being largely used is the so-called Mather-Thomson Process, which uses an improved form of apparatus. In place of using solutions of chloride of lime, the chemic is sometimes prepared by the electrolysis of a solution of common salt. This furnishes a hypochlorite of sodium, but the bleaching efficiency is said to be somewhat greater than a corresponding amount of bleaching powder solution. A similar solution can be prepared more economically and satisfactorily by the use of liquid chlorine.

This product is now largely employed in connection with soda ash or caustic soda, and most of the large bleacheries in America have adopted this method of preparing chemic for bleaching.

Linen. This is next to cotton in importance as a vegetable textile fiber. It is obtained from the *bast* of the flax plant, *Linum usitatissimum*, and differs considerably from cotton in its structure and appearance. The flax plant is grown largely for its fiber in Europe, Ireland and Russia being the chief producers. Though also grown extensively in other parts of the world, it is cultivated principally for its seed, which ultimately furnishes linseed oil. In preparing the fiber the entire plant is taken and put through a *rippling* machine for the purpose of removing the leaves, seeds, etc. The cleaned stalks are then subjected to a process known as *retting* for the purpose of decomposing the woody tissue and dissolving the resinous and gummy matters so that the free fiber may be obtained. Retting is essentially a fermentation process, and a number of different methods are employed. The two chief methods are: (1) steeping in stagnant water. The flax straw is tied into convenient bundles and laid down in pools of soft water. Fermentation rapidly sets in, and when the woody tissue has been decomposed, but before the fiber itself is attacked, the bundles are removed and spread out on the grass for a number of days, where they may be exposed to the combined action of sunlight and air.

The pulpy stalks are then passed through special breaking and scutching machines for the purpose of breaking-up and removing the decomposed matters and leaving the fiber free and clean. Flax produced in this manner has a rather dark grayish-brown color, as the coloring matters formed during the retting process are not removed. The majority of the Irish flax and some of the Russian flax is retted in this manner. (2) Steeping in fresh running water (in streams) is another method of retting by which most of the French and Belgium flax is made. The bundles of flax straw are submerged in the streams by means of crates. The fermentation proceeds more slowly than by the first method, but the coloring matters are removed by the running water, so the final product is much lighter in color, and the fiber is of a superior quality. Flax may also be retted by exposing the stalks for a number of weeks to the action of dew. There have also been a number of "improved" chemical methods proposed for the retting of flax, chiefly with the purpose of hastening the fermentation and obtaining a brighter and clearer fiber, but none of these have proved to be of any value.

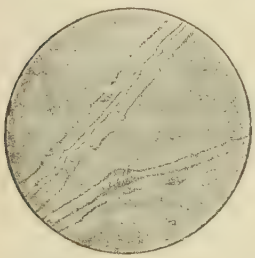

Fig. 360.—Linen Fiber.

The linen fiber as it appears in trade is in the form of long, rather coarse, filaments of a silver or brownish color. These fibers consist of a number of comparatively small elongated cells cemented together by a glutinous intercellular substance. The individual fiber cells are about 1 to 2 ins.

in length and from 12 to 25 μ[1] in diameter. The fiber is cylindrical with thick cell-walls and a narrow internal canal. Under the microscope the fiber shows the presence of peculiar cross-marks resembling joints or dislocations (see Fig. 360).

In its chemical properties linen is very similar to cotton, but its cellulose is less pure owing to the intercellular substances present. The following is an average analysis showing the composition of linen:

Water	8.65–10.70%
Aqueous extract	3.65– 6.02
Fatty and waxy matters	2.39– 2.37
Intercellular matters	2.74– 9.41
Cellulose	82.57–71.50
Ash (mineral matter)	0.70– 1.32

Linen is bleached in the same general manner as cotton, but as the fibers are more or less disintegrated into the individual cells by the bleaching process, fully bleached linen is much weaker than raw linen. On this account, linen is generally only partially bleached. In its general characteristics linen is stronger than cotton but less elastic; it is a better conductor of heat, hence linen garments are colder than those of cotton. Linen also has a higher degree of luster than cotton.

Jute. This fiber is without doubt next in commercial and technical importance to linen. It is also a bast fiber obtained from the stalks of *Corchorus capsularis*, or Jew's mallow, growing in tropical and subtropical countries. The majority of the jute of commerce comes from India and the East-Indian Islands. The fiber is prepared from the stalks by a simple retting in water, the fiber separating rather readily from the other tissues. As it appears in trade the fiber is from 4 to 7 ft. in length, usually of a yellowish-brown color, though some qualities are of a silver-gray color. It has considerable luster and a high tensile strength. The cell-elements of the jute fiber are rather small, being about 1.5 to 5 mm. in length and 20 to 25 μ in diameter. The fiber is composed of a rather large number of these cell-elements cemented together. A cross-section of the fiber shows these cells to have a polygonal outline. The microscopic appearance of the jute fiber differs from that of linen in not exhibiting the peculiar jointed ridges running across the fiber.

In its chemical composition and properties, jute differs essentially from the other vegetable fibers. Instead of being composed of relatively pure cellulose it appears to consist almost altogether of a modified form of cellulose known as ligno-cellulose or bastose. This is shown by the fact that the jute fiber gives a yellow coloration when tested with iodin-sulphuric acid reagents, whereas ordinary cellulose gives a blue color. Owing to its different chemical composition, jute behaves quite differently

[1] The expression μ indicates the thousandth of a millimeter (0.001 mm.). It is a unit extensively employed for microscopic measurements.

with the various classes of dyestuffs, as it combines directly with both acid and basic dyes, whereas cotton and linen require mordants for these colors.

Jute is extensively employed for the manufacture of sacks and bags, for the backing of carpets and rugs, for small coverings, draperies, etc.

The Minor Vegetable Fibers. There are a number of vegetable fibers which are largely used for the manufacture of cordage, mats, etc., and which can scarcely be termed textile fibers in the sense of being utilized for woven fabrics. Hemp and sisal are the principal fibers used for cordage. The former is a general name for a large number of commercial fibers of similar physical appearance and properties, and obtained from a number of different plants. Sisal is a fiber obtained from the leaf tissues of the *agave* and other similar plants. Ramie or China-grass is a bast fiber obtained from species of the nettle plant. It is a fine white and very strong fiber which would be very valuable commercially except for the difficulty with which it is obtained from the plant and from the fact that the surface of the fiber is so smooth that it lacks cohesion in spinning.

Artificial Silk. This is a fiber which is attaining considerable commercial value. It is a cellulose fiber artificially prepared from suitable solutions of cellulose by forcing the liquid through fine orifices and coagulating the cellulose as it emerges in the form of a delicate thread. There are a number of methods at present used for the production of this fiber, among which the following are the most important: (1) Pyroxylin or Chardonnet silk prepared from a solution of guncotton in a mixture of alcohol and ether; as the thread is formed the solvent is evaporated and the nitrated cellulose becomes coagulated into a continuous filament. This thread is subsequently denitrated by treatment with solutions of nitric acid, ferric chloride, and ammonium phosphate. (2) Cupra-ammonium silk is prepared from solutions of cellulose in the copper-ammonium hydrate solvent known as Schweitzer's reagent. The thread is coagulated and the metallic salts removed by a treatment with a solution of sulphuric acid. (3) Viscose silk is prepared from a solution of viscose or cellulose thiocarbonate, the thread being coagulated by passing through a solution of ammonium sulphate, and subsequently washed very thoroughly to remove the sulphur compounds that are formed in the decomposition of the viscose. These artificial silks resemble true silk very closely in general appearance, possessing even a higher luster than the latter. The fiber, however, is more wiry and harsh in nature, and its strength and durability is considerably below that of true silk. The strength of artificial silk is also greatly lessened when wetted with water. This fiber, however, has a large use in the manufacture of braids, dress trimmings, passementerie, and ornamental fabrics of various kinds where a high luster is especially desirable. Artificial silk is dyed in the same manner as cotton.

Yarns for textile purposes have also been prepared from paper pulp, the general process being to cut the thin sheet paper pulp into narrow strips, and then twisting these into yarns. Such products are Silvaline and Textilose yarns and fabrics.

CHAPTER XLIII

DYESTUFFS AND THEIR APPLICATIONS

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Textile Coloring. Textile coloring may be defined as the process or combination of processes used to fix a color or colors uniformly, and more or less permanently, upon textile material. It includes both dyeing and printing.

Dyeing. The term dyeing is sometimes given almost as broad an interpretation as textile coloring, but to be specific, it should include only those processes in which the entire body of the material being colored is immersed in the coloring bath, a greater or less period of the time required for the coloring.

Textile Printing. Textile printing is a process by means of which the coloring matters applied may be confined, by use of a printing machine, to certain portions of the material, thus producing a definite colored design. The necessary dyestuffs and chemicals are made into a paste, with starch, dextrine, and various gums, and applied to the cloth by means of copper rollers, one for each color, the cloth being finally subjected to special aging and drying processes. By this method it is possible to produce prints containing ten or more different colors.

By combined dyeing and printing many different and pleasing effects may be produced.

Staining. Staining is the term often applied to the process of coloring such materials as wood, bone, and ivory, and the coloring matter in this case is ordinarily applied with a brush.

The terms staining and dyeing are both applied to the coloring of leather, straw, paper, and feathers, their respective use depending somewhat upon the process used, but in most cases the term dyeing is more accurate.

Compounds Used by the Textile Colorist. The chemical compounds used by the textile colorist may be divided into two classes:

(1) Those which possess no coloring power, but which are instrumental in the fixation or development of coloring matters upon the fiber.

(2) Those which are true coloring matters.

First Class. Compounds Instrumental in the Fixation of Coloring Matters upon the Fiber, although Possessing no Coloring Power Themselves. The compounds included under this heading are frequently spoken of as *fixing agents*, but when used in this broad and indefinite sense, the term frequently leads to confusion rather than to enlightenment. In order to eliminate this confusion as far as possible, we will classify the most important compounds coming under this class as follows:

(1) Mordants: (*a*) Metallic. (*b*) Non-metallic. (*c*) Acid.
(2) Mordanting assistants.
(3) Chemical fixing agents.
(4) Mechanical fixing agents.
(5) Developing agents.
(6) Leveling agents.
(7) Dyeing assistants.

Mordants. Mordants in general may be defined as substances capable of uniting with certain dyestuffs to form insoluble colored compounds which under the proper conditions may be more or less permanently fixed upon textile material. They may be subdivided as *metallic, non-metallic,* and *acid mordants.*

Metallic Mordants. Metallic mordants are substances, usually metallic oxides or hydroxides, which are capable of uniting with certain dyestuffs, known as mordant dyestuffs, to form insoluble colored compounds which for the most part are known as *color lakes.*

Non-metallic Mordants. The only non-metallic mordant of importance, and this of only minor importance, is sulphur. Sulphur is sometimes used as a mordant when applying certain basic colors, e.g., malachite green upon wool.

Acid Mordants. Tannic acid and various substances rich in this acid, such as sumac, gall nuts, and various bark extracts, and less frequently various fatty acids, such as oleic and stearic acids, and Turkey red oil, are the only acid mordants of importance. Of these acid mordants tannic acid and its related compounds are the only ones commonly used, and these chiefly in the application of the basic colors to cotton material. The acid mordants are of minor importance as compared with the metallic mordants.

Mordanting Principles. As often applied, the term "mordant" indicates the soluble metallic salt used to produce the mordant, but in the proper sense the mordant is that substance, which in direct combination with the dyestuffs, forms the color lake. In order to avoid this confusion, we will designate the compound used to produce the mordant as the *mordanting principle.* Thus in one of the most common wool mordanting processes the soluble potassium dichromate is the mordanting principle, but the insoluble chromium chromate and chromium hydrate ultimately fixed upon and within the fiber constitute the true mordant.

Mordanting Assistants. Mordanting assistants are compounds such as tartar, lactic acid, oxalic acid, and sulphuric acid used in conjunction with the mordanting principles to bring about a gradual decomposition of the latter, and assist in producing a uniform deposition of the actual mordant upon and within the textile material.

Mordanting Process. The mordanting process is the operation whereby various mordants are precipitated and so deposited upon textile material that they may be subsequently united with mordant dyestuffs *in situ* to form insoluble color lakes. Through the combined mordanting and dyeing processes these color lakes become fixed upon the textile material, thus imparting to it a permanent color. Occasionally, in special cases, the dyestuffs may be applied at the same time or even previous to the mordant.

Chemical Fixing Agents. Under the heading of chemical fixing agents we will include:

First. Those substances which are instrumental in the fixation of various mordants upon textile material by uniting chemically with such mordants and holding them upon the fiber until the proper dyestuffs may be given an opportunity to unite with them. Examples: The various antimony compounds used to fix tannic acid upon cotton fiber. Various tannin compounds used to hold iron upon the fiber as the insoluble tannate of iron when the latter is to act as a mordant with logwood or other mordant dyestuffs.

Second. Those substances which cause the actual precipitation of the mordant usually by the double decomposition of the mordanting principle. Example: When cotton material saturated with nitrate of iron is passed through a solution of sodium carbonate, the basic carbonate and hydrate of iron are precipitated upon the fiber, and sufficiently fixed thereon to act as a mordant.

Mechanical Fixing Agents. These are substances (such as albumen) capable of holding pigments, permanently, upon the fiber, or certain gums and starches capable of holding dyestuffs and other substances upon the fiber a sufficient length of time to permit of some desirable reaction taking place. Their action is purely mechanical.

Developing Agents. The term developing agents is applied to organic compounds which in combination with some other organic compound already deposited upon the fiber will develop a colored compound, or if united with a dyestuff already upon the fiber will form a new coloring matter possessing a more desirable or a faster color. Examples: Beta-naphthol upon the fiber, when combined with diazotized para-nitro aniline (developing agent) will produce para red. Primuline, a yellow dyestuff, when diazotized upon the fiber by treatment with nitrous acid and then combined with beta-naphthol (developing agent) produces a bright red coloring matter.

Leveling Agents. Leveling agents are compounds added to the dye-

bath in conjunction with certain dyestuffs to assist in bringing about the level or even deposition of the latter. Example: Glauber's salt used in conjunction with the direct cotton colors.

Dyeing Assistants. Dyeing assistants are compounds which, added to the dye-bath, facilitate the dyeing process and are beneficial in one way or another. Examples: Sulphuric acid and Glauber's salt in the dyeing of acid colors.

Application of Metallic Mordants. True mordant dyestuffs can only be applied in conjunction with metallic mordants. The mordanting process is therefore of great importance, the mordant playing almost as necessary a part in the application of a mordant color as does the dyestuff itself. Of all the metals, only a few, namely chromium, iron, aluminium, copper and tin unite with mordant dyestuffs to form valuable color lakes. On account of its general applicability chromium is most frequently used. Iron and copper produce the most permanent, while aluminium and tin produce the brightest color lakes.

Mordanting of Wool. Wool has a natural affinity for certain compounds and this facilitates the mordanting process to a marked degree. When in dilute solution mordanting principles, often in a highly dissociated condition, are aided in their decomposition by this natural attraction of wool fiber, and as a result various metallic compounds (usually oxides, hydroxides or basic salts) are slowly deposited upon the fiber. This process takes place most completely in a boiling bath and in the presence of some secondary soluble compound which has already been described as a mordanting assistant.

Chromium compounds are depended upon, almost entirely, in applying mordant dyestuffs upon wool, and potassium sodium dichromate are the most important mordanting principles for this purpose. The process most frequently used consists in boiling the wool material in a dilute solution of potassium or sodium dichromate in the presence of either tartar or lactic acid, the latter compounds acting as mordanting principles. The boiling should be continued for about one to one and one-half hours in order to secure the most complete decomposition of the mordanting principle, and fixation of the mordant upon the fiber.

Mordanting of Silk. Silk, like wool, possesses a marked affinity for metallic oxides, hydroxides, and basic salts, and for this reason may be readily mordanted. The process consists in steeping the silk in a concentrated solution of the proper mordanting principle, such as the sulphate, chloride or acetate of iron, chromium, aluminium or tin, usually in a slightly basic condition, and then thoroughly washing with a large volume of water. This process may be repeated several times depending upon the depth of color to be obtained upon dyeing.

Silk possesses the property of absorbing large quantities of metallic compounds and advantage is taken of this fact in the weighting of

silk. Silk weighting and mordanting are therefore frequently closely associated.

Mordanting of Cotton. The mordanting of cotton is more difficult than that of either wool or silk owing to the entire lack of natural attraction of cotton for metallic salts, hydroxides and oxides. The methods of cotton mordanting are numerous, but may be grouped under four general headings:

(1) Combined padding, aging, and dunging process.
(2) Combined printing, aging, and dunging process.
(3) Direct chemical precipitation upon the fiber.
(4) Steam printing.

In the first method, the cloth is evenly saturated (padded) with a solution of some mordanting principle, usually an acetate of chromium, iron, or aluminium. It is then subjected to a hot moist atmosphere for a number of hours (aging) which brings about a slow decomposition of the acetate with fixation of metallic oxide upon the fiber, and liberation of acetic acid. The fixation of the mordant, and neutralization of the free acid present is brought about by the dunging process which consists in thoroughly treating the aged material in a bath made up with such substances as phosphates, silicates, and carbonates of potassium, sodium, ammonium, and calcium. Sodium arsenate is a valuable fixing agent for this purpose but its use has been largely discontinued owing to the poisonous nature of the arsenic.

The second method differs from the first only in that the mordanting principle is printed upon the fabric rather than padded.

The third method consists in the direct chemical precipitation of the mordant upon the fiber. In this method the material is first padded with the mordanting principle and then passed through a bath containing the precipitant.

In steam printing the mordanting principle and mordant dyestuff are mixed together with the proper thickening agents and then printed upon the cloth. Upon steaming, the mordanting principle decomposes and forms the mordant which unites with the coloring matter *in situ*.

Owing to the shortage of coal tar colors, brought about by the European war, the natural dyes, which are for the most part mordant dyes, have been extensively used during the past two or three years. This has led to considerable experimentation in the application of metallic mordants to cotton. One of the most important advances along this line has been the introduction of D salt.[1] By boiling cotton material in

[1] D salt is a preparation so-called after its discoverer, W. C. Durfee. It is apparently a colloidal solution of chromium dioxide together with sufficient chromic acid to establish an equilibrium which although comparatively stable at ordinary temperature, is easily disturbed through boiling in the presence of textile material or when dried upon textile material, with a resulting deposition of a stable chromium mordant.

a solution of this salt it is readily mordanted with a chromium mordant.

Second Class. Coloring Matters and Dyestuffs. In general, a coloring matter is a substance which if properly used will impart a characteristic color to some other substance. By common usage the term dyestuff is almost synonymous with that of coloring matter, particularly as applied to textile material.

Classification of the Dyestuffs. The earliest classification of dyestuffs was made by Bancroft, who divided them into two classes, *substantive* and *adjective*. He designated as substantive dyestuffs those capable of producing a fully developed color upon textile material without the necessary assistance of any other combining substance, and as adjective dyestuffs those requiring an intermediate combining substance (*called a mordant*) to satisfactorily fix and fully develop the color. This grouping is still in use, but during recent years, the tendency has been to use the term, *direct color* instead of substantive, and *mordant color* instead of adjective. In general the classification holds true; but there are instances where dyestuffs are substantive toward one fiber, but adjective toward another. This is well illustrated by the basic colors which will dye wool directly but require a mordant upon cotton.

The *classification which divides the dyestuffs according to their origin is* of broader application. It recognizes three groups and is as follows:

(1) *Natural Organic Dyestuffs.* Including (*a*) *Vegetable;* (*b*) *Animal.*
(2) *Mineral Dyestuffs.*
(3) *Artificial Organic Dyestuffs.*

Though the various subdivisions of this classification, particularly of the artificial organic dyestuffs, are numerous and varied in the character of the dyestuffs they include, this general classification has the advantage of conciseness, and one class does not overlap another.

The natural organic dyestuffs include such coloring matters as logwood, indigo, fustic, cutch, and cochineal.

The mineral coloring matters include Prussian blue, chrome yellow iron buff and a number of other inorganic pigments.

The artificial organic dyestuffs are the most important and this class may be divided into twenty or more important sub-classes. They include all of the so-called coal-tar dyes, such as magenta, benzo-purpurine, acid violet, tartrazine, and the alizarines.

Natural Organic Dyestuffs. For convenience we shall subdivide the natural organic dyestuffs as follows:

(1) Indigo and related compounds.
(2) Logwood.
(3) Natural dyestuffs producing shades of a red character.

(4) Natural dyestuffs producing shades of a yellow to brown character.

Indigo. Indigo blue or indigotin occurs in many plants, chiefly those of the genus *Indigofera*, the *Indigofera tinctoria* yielding the largest quantity. The Indigofera thrive only in tropical climates, and for several hundred years the cultivation of the indigo plant was one of the chief industries of Southern Asia, particularly India and Java. The introduction of the artificial indigo however has dealt a severe blow to the natural indigo industry, and the synthetic indigo now seems likely to entirely replace the older vegetable product.[1]

The indigo plant is herbaceous in character, grows 3 or 4 ft. high, and with a stem about $\frac{1}{4}$ in. in diameter.

Indigo blue, or *indigotin* as it is known chemically, does not exist as such in the plant, but is developed through the indirect decomposition of a glucoside known as indican. When the leaves and stems are steeped in water and allowed to ferment, a clear yellow liquid results which contains the indigo as the soluble indigo white. When this liquor is violently agitated, so as to expose all parts to the action of the oxygen of the air, the soluble indigo white is converted into the insoluble indigo blue. This is allowed to settle, pressed into cakes, and when dry is ready for the market.

Chemistry of Indigo Dyeing. Indigo differs from the majority of dyestuffs in that it is insoluble in all of the reagents which the dyer can employ practically, but nature has fortunately given it a property which renders its application comparatively simple. When reduced in an alkaline bath, it is easily converted into the soluble indigo white as follows:

$$\underset{\text{Indigo blue}}{C_{16}H_{10}N_2O_2} + 2H = \underset{\text{Indigo white}}{C_{16}H_{12}N_2O_2}.$$

Upon even the mildest oxidation, indigo white passes back to indigo blue as follows:

$$\underset{\text{Indigo white}}{C_{16}H_{12}N_2O_2} + O = \underset{\text{Indigo blue}}{C_{16}H_{10}N_2O_2} + H_2O.$$

Indigo white being readily soluble in alkaline water solution, and this solution being easily absorbed by both animal and vegetable fibers, the process of application becomes comparatively simple. Upon exposure of the saturated fiber to the air, the indigo white is oxidized almost immediately to the insoluble indigo blue, which is rapidly precipitated upon and within the pores of the fiber to as great a depth as the indigo white solution has penetrated. The alkaline bath of indigo white is commonly

[1] During the European war the supply of synthetic indigo has been practically shut off and as a result the natural indigo industry has revived but this is undoubtedly only a temporary condition.

called an *indigo vat*, and this process of coloring is usually spoken of as *vat dyeing*.

Application of Indigo. Indigo is extensively used for the dyeing of cotton and wool, but seldom for silk.

Three forms of indigo vats are chiefly depended upon at the present time:

(1) Fermentation vats.
(2) Zinc lime vats.
(3) Hydrosulphite vats.

These vats all involve the principle of reducing finely ground indigo to indigo white, and differ only in the methods used to bring about this reduction.

The *fermentation vat* is the oldest, but is still frequently used in wool dyeing, although never used for cotton dyeing. The reduction in this case is brought about by the fermentation of various organic substances such as bran, woad, molasses, and madder in an alkaline solution.

The *zinc lime vat* has been used largely for cotton dyeing, but not for wool dyeing. The reduction in this case is brought about by the action of zinc powder upon water in the presence of an alkali, that alkali being calcium hydroxide. The reaction may be represented by the following equation

$$Zn+2H_2O=Zn(OH)_2+2H.$$

The *hydrosulphite vat* is the most recent of the indigo reduction vats, and has largely replaced the fermentation vat for wool dyeing, and the zinc lime vat for cotton dyeing. In this vat the reduction is brought about by means of a sodium hydrosulphite solution, which is commonly prepared just before use by the action of zinc dust upon sodium bisulphite solution. The reactions may be represented by the following equations:

$$2NaHSO_3+Zn=Na_2S_2O_4+Zn(OH)_2$$
$$Na_2S_2O_4+2H_2O=2NaHSO_3+2H.$$

The application of indigo to *cotton and wool* differs chiefly in the fact that it is more difficult to penetrate wool than cotton with the indigo white solution and thus a longer period of immersion and a somewhat higher temperature is required.

Cotton requires an immersion of only a minute at ordinary temperature, unless the material is heavy, while wool requires from twenty minutes to an hour at a temperature of 120° F.

Indigo Extracts. These are prepared by the action of concentrated sulphuric acid upon indigo blue. The resulting compounds are the indigotin sulpho acids, which are freely soluble in water, and may be easily applied to wool in an acid bath. They dye wool a brighter blue

than ordinary indigo, but unfortunately the dyeings produced are extremely fugitive to light, whereas vat indigo on wool produces one of the fastest blues known. The use of the former is very much restricted for this reason. The indigo extracts are of no value for cotton dyeing.

Logwood. Logwood is the product of a large and rapidly growing tree known botanically as the *Hæmatoxylin campechianum.* It is a native of Central America and the adjacent islands, Jamaica being one of the chief centers of the logwood industry. Raw logwood, as the name implies, comes in the form of rough logs, which are ground or rasped into small chips. It may be used in this latter form after it has been properly aged, but during recent years it has been more frequently put upon the market in the more concentrated form of an extract.

Chemistry of Logwood Coloring. Careful examination of freshly cut logwood chips reveals the presence of a yellowish-crystalline compound having the empirical formula $C_{16}H_{14}O_6$ and to which the name *hæmatoxylin* has been assigned.

When exposed to the air hæmatoxylin, especially in the presence of an alkali, rapidly oxidizes to a reddish-brown substance known as *hæmatein* and having the empirical formula $C_{16}H_{12}O_6$. Hæmatein is the active coloring matter of logwood. Upon further oxidation it passes into a resinous brown substance which is of no value for coloring purposes.

Logwood is in every sense of the word a mordant dyestuff, a metallic mordant being required to satisfactorily fix the dyestuff upon any textile fiber. During the dyeing process the hæmatein of the logwood unites with the mordant to form an insoluble metallic organic compound or color lake, which becomes fixed upon the fiber.

The chief metals entering into these color lakes are chromium, iron, aluminium, and copper. Logwood is commonly classified as a black dyestuff, and is used chiefly for the production of blacks, but more strictly speaking, it is a blue dyestuff, for with both aluminium and chromium, it produces blue dyeings and although with iron the shade produced approaches black, it is customary to add a small amount of some yellow or brown dyestuff to produce a satisfactory black.

Aging of Logwood. In general, logwood, when ready for the dyer, should contain a high percentage of hæmatein, but little unoxidized hæmatoxylin, and none of the resinous brown oxidation product already mentioned.

In order that this ideal condition may be approached as nearly as possible, logwood must be aged.

Logwood chips are commonly aged as follows:

After having been made into a large pile several feet in depth, the chips are well moistened with water, and then worked over with wooden shovels, every portion of the pile being thus brought in contact with the air. This is continued for a period of from three or four days to two weeks, depending largely upon atmospheric conditions. After some

experience, one can tell, from the appearance of the chips when the right stage of oxidation is reached. The chips are then stored in such a way as to be exposed as little as possible to the oxidizing influence of the air.

When aged logwood is known to contain much hæmatoxylin, and consequently incompletely aged, the aging may be continued to a certain extent during the dyeing process by adding some oxidizing agent or using an oxidizing mordant, e.g., chromium in the CrO_3 form.

Logwood Liquor. Logwood liquor is a decoction of logwood made by extracting aged logwood chips with water. It usually has a strength of 15° Tw. (Sp.gr. 1.075) and as it does not keep well is only made as required for use.

Logwood Extracts. At the present time, logwood is most frequently put upon the market in the extract form. Logwood extracts are made by evaporating logwood liquor in vacuum pans until it reaches a sp.gr. of 1.25 or 50° Tw., or it may be carried to dryness to produce the solid extracts.

These solid extracts are prepared by patented processes. They vary somewhat in strength and chemical character, and are frequently designated as *hæmatine crystals.*

Application of Logwood. Logwood is still used in *wool dyeing* on account of its cheapness, and because the characteristic bloomy blue-black which it gives is difficult to produce at as low a cost with coal-tar coloring matters. In wool dyeing, logwood is chiefly used in conjunction with a chromium mordant, a small amount of some yellow or brown dyestuff, frequently fustic, being combined with it, to overcome the pronounced bluish cast which would otherwise result.

One dip logwood blacks are prepared by using in conjunction with logwood some mordanting principle, and a sufficient quantity of an acid, usually oxalic, to prevent too rapid precipitation of the color lake. A mixture frequently used for this purpose consists of logwood extract, ferrous sulphate, copper sulphate, and oxalic acid.

The use of logwood upon *cotton* has greatly diminished during recent years, logwood blacks having been largely replaced by aniline black, sulphur blacks, and certain direct cotton blacks. When used upon cotton it is most frequently applied in conjunction with an iron mordant, either alone or in combination with a copper mordant.

Logwood is extensively used for the production of blacks upon *silk.* Iron mordants are depended upon almost entirely for this purpose and tin mordants occasionally. The process usually consists in alternately treating the silk with some tannin material, and an iron or a tin compound until the silk is thoroughly filled with the metallic tannate. The silk thus mordanted is then dyed in a logwood bath. By using tin compounds in conjunction with acetate of iron it is possible to weight black dyed silk as much as 300 per cent of its original weight.

Soluble Red Woods. Brazil wood, peach wood, Japan wood, and Lima

wood are the principal soluble red woods. They are all mordant colors, and may be applied to mordanted cotton or wool by boiling in a plain bath of the extracted color.

Insoluble Red Woods. These include barwood, Saunders wood, and camwood. On account of the insolubility of the coloring matters which they contain, the ground or rasped chips of wood must be added directly to the dye bath. They are all mordant colors. The red woods have been replaced by coal-tar colors which give more permanent and clearer dyeings at a lower cost. Hypernic extract is prepared from a mixture of red woods.

Madder. Madder root, which was known to the ancients, was for many hundreds of years the most important of the red natural coloring matters, and was used chiefly in the production of Turkey reds. The active coloring principle of madder is alizarine $C_{14}H_8O_2$, and the discovery in 1868 by Graebe and Liebermann that alizarine could be cheaply made from coal-tar derivatives soon led to the abandonment of madder as a coloring matter except in the Oriental countries where it is native.

Cochineal. Cochineal is a red mordant coloring matter obtained from the dried body of an insect which is native of Mexico and Central America. In the past, cochineal was extensively used for the production of scarlets and crimsons on wool in conjunction with tin and aluminium mordants. Like most of the other natural colors, cochineal has been superseded by the artificial dyestuffs.

Other red natural dyestuffs worthy of mention are kermes, and lac dye, which are similar to cochineal in origin, though of less importance; also orchil and cudbear bluish-red coloring matters, which like litmus are derived from certain rock mosses or lichens.

Natural Dyestuffs of a Yellow to Brown Color. *The yellow natural dyestuffs* include a number of vegetable dyestuffs which vary between yellow and brown. Fustic, quercitron bark, Persian berries, turmeric, weld, and cutch are the most important.

Fustic or Cuba Wood. Fustic or Cuba wood is the most important of the yellow dyewoods and is still used to some extent in wool dyeing, chiefly in combination with logwood. It is a mordant dyestuff, being used with chromium and aluminium mordants. It possesses excellent fastness. It is sold in the form of ground wood, but more frequently as an extract.

Osage Orange is a comparatively new dyewood. The wood of the osage orange tree, which grows in the southern part of the United States, is extensively used in the manufacture of wagon wheels, and it has been discovered that an extract made from the sawdust and waste possesses dyeing properties almost identical with fustic, both as to color produced and fastness.

Quercitron Bark. Quercitron bark is obtained from the bark of a species of oak which grows in the Middle and Southern States. It is a

mordant color and gives brighter yellows than fustic. Its use is limited at the present time.

Persian Berries. Persian berries is the name applied to the berries of the buck-thorn. In the extract form it is used to a limited extent in calico printing.

Turmeric. Turmeric is the ground root of a plant which grows in Asia. It dyes cotton, wool, and silk bright shades of yellow which are extremely fugitive to light and washing.

Cutch or Gambia. Cutch or gambia, a coloring matter rich in tannin, is extracted from the nuts and tender portions of various forms of acacia trees growing chiefly in India. It is used chiefly for the production of browns upon cotton also as a tannin material in silk dyeing.

Mineral Dyestuffs. The mineral dyestuffs as a class are of minor importance in the textile industry. Various mineral pigments are sometimes used in calico printing, but in the actual dyeing process the only mineral dyes of any importance are Prussian blue, chrome yellow, chrome green, iron buff, and khaki.

Prussian Blue. Prussian blue may be produced upon textile material by one of two methods. The first consists of mordanting the material with iron oxide, and then boiling in a solution of potassium ferrocyanide. The second method makes use of the fact that both the ferro and ferri cyanides of potassium decompose when boiled in an acid solution and from such a boiling solution Prussian blue is absorbed by textile material. The first process is used chiefly with cotton while the second is better adapted to wool dyeing.

Chrome Yellow. Chrome yellow is the yellow lead chromate which may be precipitated upon the fiber by alternate treatments with solutions of some soluble lead salt and a chromate.

Chrome Green. Chrome green is a basic oxide of chromium precipitated upon the fiber by the reaction of some soluble chromium salt with an alkali.

Iron Buff. Iron buff is a ferric hydroxide precipitated upon the fiber by the reaction of some soluble iron salt with an alkali.

Khaki. Khaki is a yellowish drab color produced by the precipitation upon the fiber of a combination of ferric hydroxide and basic chromium hydroxide. Khaki when properly dyed produces an extremely fast color.

Artificial Organic Dyestuffs. The natural dyestuffs were depended upon almost wholly until the discovery of *mauve* by Perkin in 1856. Mauve was the first of the so-called coal-tar dyes, or better manufactured organic dyestuffs. Its discovery was followed by that of many similar dyestuffs, and a new era soon began in the textile coloring industry. To-day well toward a thousand entirely different dyestuffs of this class are at the disposal of the textile colorist and from them we can select dyes which will answer almost every requirement of shade and fastness.

Classification of the Artificial Organic Dyestuffs. The artificial organic dyestuffs may be classified according to their chemical derivation, their composition, or in respect to the characteristic color-forming groups which they contain. While these classifications prove very satisfactory for the color-manufacturing chemist, they prove of little or no value to the practical textile colorist. Another classification which groups them according to their action toward the various textile fibers, i.e., according to their application, is by far the most practical and valuable for the student of textile coloring, and will be followed. It recognizes ten classes of coloring matters:

(1) Basic colors.
(2) Phthalic anhydride colors.
(3) Acid colors.
(4) Direct cotton colors.
(5) Sulphur colors.
(6) Mordant colors.
(7) Mordant acid colors.
(8) Insoluble azo colors. Produced directly upon the fiber.
(9) Reducible vat colors.
(10) Miscellaneous colors.

Basic Colors. Chemically the basic dyestuffs belong to the class of compounds known as substituted ammonias or amines. Like ammonia they are basic in character, and hence the name.

The basic colors have a direct affinity for wool and silk, but no direct affinity for cotton, and can only be applied to the latter fiber in conjunction with some acid mordant, usually tannic acid.

Application of Basic Colors to Wool. Although the basic colors have a direct affinity for wool, they are not extensively used in wool dyeing, for in most cases there are more desirable acid dyes. When applied to wool it is customary to boil the material in a bath made up with the required quantity of dyestuff, sufficient acetic acid to render the bath distinctly acid, and Glauber's salt equal to 10 per cent of the weight of material being dyes.

Application of Basic Colors to Silk. The basic colors have a direct affinity for silk, and are extensively used for dye ng this fiber when bright rather than fast colors are desired. The dye bath is made up with 25 per cent "boiled off liquor"[1] and the remainder with water to which is added the required quantity of dyestuff and sufficient sulphuric, acetic, or tartaric acids to render the bath slightly acid. The silk material is entered at 100° F., the temperature of the bath then raised to 140 F.

[1] Preliminary to dyeing, silk is subjected to the "boiling off" or "degumming process." The liquor resulting from this operation is known as "boiled-off liquor."

the material worked at this temperature for a few minutes, and the bath finally raised to a boiling temperature.

With dyestuffs which go on the fiber unevenly it is advisable to lift the silk material from the bath while the temperature is being raised.

Application of the Basic Colors to Cotton. Although the basic colors have no direct affinity for cotton, it is for the dyeing and printing of this fiber that they find their most extensive application. Before dyeing cotton material it must first be impregnated with tannic acid, and this fixed upon the fiber as an insoluble metallic tannate usually of antimony. When such a tannin mordanted cotton material is dyed in a bath containing a basic color, an insoluble combination of the dyestuff, tannic acid, and antimony results, which becomes fixed upon the fiber. In calico printing, the basic color and tannic acid are mixed together in the printing paste, and chemical combination between the two is brought about by a subsequent steaming process. More thorough fixation of color may be obtained by after-treating the printed and steamed cloth with some soluble antimony compound, usually tartar emetic.

Characteristic Properties of the Basic Colors. The basic colors are characterized by their great brilliancy and high coloring power. Their fastness to light is by no means satisfactory, but their fastness to washing in most cases is very good.

The Phthalic Anhydride Colors. The phthalic anhydride colors are so called because they are directly related to this compound. They include the eosines and rhodamines, and are extensively used for the production of bright pinks, particularly in silk dyeing, and less frequently in wool dyeing. They are not used to any great extent in cotton dyeing, although sometimes used in cotton printing. The rhodamines are closely related to the basic colors and may be applied in a similar manner.

Application to Wool. The phthalic anhydride colors are applied to wool in conjunction with alum, potassium bitartrate, and acetic acid.

Application to Silk. These colors are applied similarly to basic colors.

Application to Cotton. In calico printing the phthalic anhydride colors are either applied in a similar manner to basic colors, or in conjunction with aluminium acetate.

Characteristic Properties. The phthalic anhydride colors are characterized by their remarkable brilliancy.

Acid Colors. The acid colors are so called on account of their acid character, and furthermore because they dye wool so readily in an acid bath. They are of great importance in wool dyeing, about 75 per cent of all wool dyeing being accomplished at the present time by their use. The acid colors are also extensively used in silk dyeing, but are of no importance in cotton dyeing.

From a chemical point of view the acid colors may be subdivided according to their composition into three classes: (1) Those which are nitro compounds, i.e., those containing the nitro or NO_2 group. (2)

The sulphonated basic colors, i.e., those made by treating basic colors with concentrated sulphuric acid, and thereby introducing the sulphonic acid or HSO_3 group. (3) Those which are azo colors, i.e., those containing the azo or —N=N— group. The dyestuffs of the third group are the most numerous and most valuable of the acid colors.

Application to Wool. The acid dyestuffs, almost without exception, are absorbed readily by wool in an acid bath and the dyeing process is comparatively simple. The dyebath is prepared with the required quantity of dyestuff, Glauber's salt equal to 15 per cent,[1] and sulphuric acid equal to 3 to 5 per cent of the weight of the material being dyed. Instead of this mixture of Glauber's salt and sulphuric acid, a corresponding amount of sodium bisulphate may be used. The material is entered at a temperature of about 140° F., brought slowly to a boil, and dyed at a boiling temperature for three-quarters of an hour, or longer if much dyestuff remains in the bath. With some acid dyes better results are obtained by substituting acetic acid for sulphuric acid, particularly at the beginning of the dyeing process. When acetic acid is used about 2% of sulphuric acid is usually added toward the end of the dyeing process.

Application to Silk. In silk dyeing the proper quantity of dyestuff is added to a bath, made up with " boiled-off liquor " and water, to which has been added sufficient sulphuric acid to render the bath decidedly acid. The dyeing is begun at 100 to 125° F., and the bath slowly raised to 200° F., but no higher.

Application to Cotton. The acid dyestuffs have no affinity for cotton, and although occasionally used for special purposes they need not be considered in this respect.

Properties of Acid Dyestuffs. The number of the acid dyestuffs is so great and their properties so varied that it is difficult to describe definite properties that will apply to all.

Most of the acid colors are easily soluble in water, and, from an acidified water solution, animal fibers rapidly, and in many cases completely, absorb the dyestuff. The vegetable fibers, in general, have no direct affinity for the acid colors; jute, however, as an exception, has a slight affinity for a few special colors.

Direct Cotton Colors. The direct cotton colors, as their class name indicates, have a direct affinity for cotton. All vegetable fibers readily absorb the direct cotton colors from their simple water solution, but for practical results it is advisable to make certain other additions to the dye bath. The direct cotton colors also dye the animal fibers directly but in most cases acid colors are preferred. The direct cotton colors having a direct affinity for both animal and vegetable fibers find extensive application in the dyeing of *union material* composed of cotton and wool, or cotton and silk.

[1] The percentage referred to here as in all other cases in this chapter is based upon total weight of material being dyed and not on concentration of solution used.

Application to Cotton. The direct cotton colors are usually applied to cotton material by boiling for one hour in a dye-bath made up with the necessary quantity of color, and Glauber's salt or common salt to the extent of 10 to 30 per cent of the weight of material being dyed. In some cases it is advisable to add from 1 to 3 per cent of soda ash, the quantity added varying with the amount of dyestuff used. In the dyeing of delicate tints, and with material which is difficult to penetrate, soap is sometimes added to the bath, and sodium phosphate used instead of Glauber's and common salts. It is always advisable to keep the bath as short, i.e., as concentrated, as possible, when applying these colors to cotton. An after-treatment with copper sulphate or potassium dichromate solution renders certain of the direct cotton colors somewhat faster to light.

Cotton material dyed with certain direct cotton colors, particularly blacks, blues, and browns, may sometimes (depending upon their composition) be rendered much faster to washing and increased in intensity of color by the process known as *diazotizing* and *developing*. To accomplish this, the material, which has already been dyed by one of the regular methods, is rinsed in cold water, and diazotized by working fifteen to twenty minutes in a cold bath of dilute sodium nitrite. After removal from this bath the material is again rinsed in cold water and worked for fifteen minutes in a bath containing the proper developer.[1]

Application to Wool. Wool may be dyed with most of the direct cotton colors in a neutral bath with or without the addition of Glauber's salt or common salt.

In some cases it is advisable to add a little acetic acid, but the addition of too much acid causes the dyestuff to go upon the fiber unevenly.

Application to Silk. The direct cotton colors are applied to silk in much the same manner as to wool. The addition of "boiled-off liquor" is an advantage.

Application to Cotton and Wool Union Material. The direct cotton colors having a direct affinity for both cotton and wool are extensively used in the dyeing of union goods. By the choice of proper dyestuffs, and regulation of process, chiefly through variation of temperature, almost any color can be produced upon such material in one bath.

Properties of the Direct Cotton Colors. The direct cotton colors vary greatly in fastness. In general, they are not fast to washing when applied to cotton although much faster in this respect upon wool. Many of the reds are extremely sensitive to acid.

The property known as "bleeding" is one of the valuable as well as one of the detrimental characteristics of the direct cotton colors.

This property is valuable since it tends to produce very level dyeings, and also to correct unevenness. On the other hand it is detrimental as

[1] Beta-naphthol dissolved in the necessary quantity of caustic soda solution is most frequently used for this purpose.

it prevents the use of the direct cotton colors for coloring of ginghams and in calico-printing.

The direct cotton colors are, as a rule, readily soluble in water.

Sulphur Colors. The sulphur or sulphide colors, as they are frequently called, are in many respects similar to the direct cotton colors, but differ so entirely in many other respects that they are grouped by themselves. In recent years they have become an important factor in cotton dyeing, on account of the fastness of the dyeings they produce, and they are now extensively used for the production of fast blacks, blues, browns, and compound shades upon cotton.

They are called sulphur colors for three reasons: In the first place, sulphur is a constituent of all of the dyestuffs of this class; sulphur and sodium sulphide are largely used in their manufacture; and finally, sodium sulphide is almost without exception a necessary constituent of the dye-bath during their application.

Application of the Sulphur Colors. The sulphur colors are only used in the dyeing of vegetable fibers, the strongly alkaline sodium sulphide bath which must be used to hold the color in solution prohibiting their use with animal fibers.[1] In general they are applied in a bath made up as follows: Dyestuff from 1 to 20 per cent of the weight of the material, sodium sulphide one to four times the weight of dyestuff, soda ash 5 to 10 per cent, and Glauber's or common salt 20 to 50 per cent of the weight of material being dyed. The material to be dyed is entered at or just below the boil, and dyed at this temperature for one hour. It is advisable to keep the textile material below the surface of the liquor as much as possible.

Properties of the Sulphur Colors. The most valuable property of the sulphur colors is their fastness to light, washing, and acids. Their fastness to chlorine and bleaching, however, is in most cases, not good.

Nearly all of the sulphur colors are insoluble in water, but dissolve readily in a solution of sodium sulphide. Copper vessels must not be used for their solution or in their dyeing as the sulphide present rapidly acts upon the copper, coating it with the black copper sulphide.

The shades produced by the sulphur colors are mostly of a dull character, and blacks, browns, dark blues, dark greens, and dull yellows; also various compound shades of these, such as drabs, slates, olives, and grays predominate. Sulphur yellows and greens as a rule do not equal the other sulphur colors in fastness. As yet no bright sulphur reds have been prepared.

Artificial Mordant Colors. The true mordant dyestuffs included under this heading cannot be permanently fixed upon cotton, wool or silk, except in conjunction with some metallic mordant. The nature of these metallic mordants and the methods of their formation upon textile mate-

[1] Special methods have been proposed for applying sulphur colors upon wool, but none has as yet come into practical use.

rial have already been described (see page 1008). They are usually fixed upon the textile material as insoluble hydroxides of chromium, aluminium, and iron, and less frequently tin and copper. During the dyeing process which follows the mordanting, the mordant dyestuffs, which contain either hydroxyl (OH) or carboxyl (COOH) groups in their composition, react with the mordants in much the same manner as acids react with bases, the result being the formation of insoluble metallic organic compounds of salt-like character which are known as *color lakes*. This reaction takes place *in situ* and the color lake is thus fixed upon and within the fiber.

Application to Wool. The material, which has already been mordanted (see page 1010), is thoroughly washed and then dyed in a bath made up with the necessary quantity of dyestuff and acetic acid. The latter is added to counteract any hardness or alkalinity of the water, and should be slightly in excess.

The dye-bath should be at ordinary temperature when the material is entered, but the temperature should be slowly raised to a boil, and the dyeing continued at a boiling temperature for one and one-half hours. This prolonged boiling is necessary in order that complete chemical reaction may take place between mordant and dyestuff.

Application to Cotton. Cotton material mordanted by one of the methods already described may be dyed by simply boiling in a bath containing the mordant dyestuff, but it is more often the case that mordant dyestuffs are applied to cotton in conjunction with some mordanting principle by the steam printing process. (See page 1007.)

Application to Silk. The mordant dyestuffs may be applied to mordanted silk but are seldom used for this fiber unless extreme fastness to soap and washing is desired.

Properties of Mordant Dyestuffs. While most of the artificial dyestuffs are soluble in water, and sold in a powdered condition, the mordant dyestuffs are the exception, being nearly all insoluble in water and sold as liquid pastes, which usually contain 20 per cent of coloring matter and 80 per cent of water. Alizarine is the most important of the mordant dyestuffs, and many of the other dyestuffs of this class are direct derivatives of alizarine. For this reason the mordant dyestuffs, as a group, are sometimes designated as the "alizarines." The mordant dyestuffs are characterized by their great fastness both to light and washing as well as all of the common color-destroying agencies.

Mordant-acid Colors. The dyestuffs of the group known as the mordant-acid colors are intermediate in general character between the acid dyestuffs and the mordant dyestuffs. They resemble acid colors in a general way, dyeing wool directly in an acid bath, but at the same time resemble the mordant colors, in that they may be applied to advantage in conjunction with metallic mordants.

During recent years, the number of mordant-acid colors has greatly

increased, and at the present time they are receiving much attention in wool dyeing, having replaced the mordant colors to a certain extent. Their popularity lies in the ease with which they may be applied, and the fact that an after-treatment with some mordanting principle converts them into color lakes possessing excellent fastness to light, acids, washing and soaping.

Application of Mordant-acid Colors. It is only upon wool that the mordant-acid colors are useful. They are dyed in the same manner as acid colors, but after the dyeing is completed the material is raised from the bath; from 1 to 3 per cent of potassium dichromate added and the boiling continued for from one to one and one-half hours. With some dyestuffs it is better to after-treat with the potassium dichromate in a separate bath, and in some instances a small quantity of some mordanting assistant, such as tartar or lactic acid, may be added to advantage.

Properties of the Mordant-acid Colors. The mordant-acid colors when properly applied approach almost if not quite the fastness of the straight mordant colors. Difficulty is sometimes experienced in producing the exact shade desired, because the color produced at the end of the dyeing is often greatly changed during the after-treatment. It is not infrequent that a yellow or red will produce a dark blue, green or even black upon after-treatment.

As the after-treatment is almost without exception carried out with potassium dichromate, the mordant acid colors are often called "chrome colors."

Insoluble Azo Colors. A number of coloring matters of the azo type exist, the insolubility of which renders them non-applicable by any of the methods already described. Fortunately the nature of the process of their formation is such that they may be produced directly upon the fiber. Many insoluble azo colors may be produced, but only two, the so-called *para-nitraniline*, and *alpha-naphthylamine reds* have proved to be of practical value. These have been extensively used upon cotton during the past twenty years, the former having replaced Turkey-red to a great extent.

The dyestuffs of this class are also known as *developed colors*, because they are developed during the process of application, *ice colors* because ice is used to attain a low temperature during their formation, and *ingrain colors* because they are formed within the grain of the fiber.

The formation of the insoluble azo colors depends upon the fact that certain diazotized amino compounds produce insoluble coloring matters when brought into contact with certain naphthols or phenolic bodies. Para-nitraniline red, the most important example, is produced by padding cotton cloth with sodium beta-naphtholate, prepared by dissolving beta-naphthol in caustic soda solution, and then passing the cloth thus prepared through a bath containing a cold solution of diazotized para-nitraniline, the latter being prepared by the action of nitrous acid upon para-nitraniline hydrochloride. As soon as the cloth prepared as above comes

in contact with the para-nitraniline solution, a bright red develops which possesses excellent fastness to light and washing. If diazotized alpha-naphthylamine is substituted for the para-nitraniline, a claret red color is produced of corresponding fastness. Para-nitraniline red on cotton is faster than any of the direct cotton reds of similar character and as regards fastness to light is exceeded only by Turkey red.

The insoluble azo colors are not applicable to wool, owing to the fact that a strong caustic soda solution must be used in dissolving the naphthol which would act injuriously upon the fiber.

Reduction Vat Colors. The reduction vat colors have come into great prominence during recent years owing to their great resistance to practically all of the color-destroying agencies, particularly light and washing. The chemistry of their application is the same as that of indigo, in fact indigo is a reduction vat color in every sense of the word. As a class these colors are insoluble in water, but when strongly reduced in an alkaline bath they form soluble, usually colorless or almost colorless, reduction compounds which are easily absorbed by the fiber. Upon subsequent oxidation the reduced compounds pass back to the original insoluble dyestuff which becomes fixed upon the fiber.

From the point of view of composition, the reduction vat colors may be divided into two classes: *first*, those directly *related to indigo; secondly*, those *related to anthracene*. The former may in most cases be applied to both cotton and wool, but the latter only to cotton.

Another important group of coloring matters of recent development are the so-called *sulphurized vat dyes*. In their properties, they may be considered as intermediate between the vat colors and the sulphur colors. But little is known in regard to their composition. The dyestuffs known as *hydron colors* belong to this group.

The coloring power of the reduction vat colors is weak and a comparatively large amount must be used in most cases. They all possess excellent fastness to washing but their fastness to light is more variable. Commercially the reduction vat colors are variously known as indanthrene, algol, helindone, ciba, thio indigo and hydron colors.

Aniline Black. *Aniline black* is usually classified as one of the *miscellaneous colors*, for it does not belong to any of the other groups. It is, in reality, an insoluble black pigment produced by the oxidation of aniline.

When aniline is oxidized, three consecutive products are formed: (1) *Emeraldine*, a greenish-colored salt insoluble in water. (2) *Nigraniline*, formed by the oxidation of emeraldine, and (3) *Aniline black proper*, or ungreenable black, as it is sometimes called, which is formed by a still further oxidation of nigraniline. The composition of the final product is not definitely known.

Aniline black is extensively used in calico-printing and the dyeing of hosiery, but cannot be used successfully in wool dyeing.

In general, aniline black is applied by preparing or printing the material with a mixture of aniline hydrochloride and certain oxidizing agents and oxygen carriers, such as potassium chlorate, potassium ferrocyanide, copper sulphide, or vanadium salts, and subsequently drying and aging it by passing through an aging chamber.

Aniline black is extremely fast to light, bleaching and washing.

The Mechanism of Dyeing. In the dyeing of textile material we have the following types of material with which to deal:

1. Raw Stock. Including loose cotton, loose wool or any other fiber in the uncarded or unspun state.

(1*a*) Carded or partly spun fiber in the form of slubbing, tops and roving.

2. Yarn in the form of skeins, and continuous chains of warp.

3. Piece goods or woven cloth.

In the older methods the dyeing process was carried out by hand. The raw stock was worked, turned over, and more or less constantly kept in motion by long poles. The yarn was dyed in the form of skeins which were suspended above the rectangular dye tubs by means of cross sticks and the skeins were frequently turned end for end and the sticks moved back and forth from one end of the tub to the other.

While these processes are still used especially for the dyeing of loose wool, most dyeing is now done by means of machines.

These machines are of two types, first, those in which the material being dyed is circulated through the dye liquor which is more or less stationary and second, those in which the material being dyed remains stationary and the dye liquor is forced through it, usually by means of rotary pumps or propeller blades.

Cloth, warps and skeins are more frequently dyed by the first method, while raw stock, tops and slubbing are most frequently dyed by the latter.

In recent years, many machines have been devised for dyeing yarn in the form of beams of warp [1] and cops [2] in order to save handling and rewinding. While in some instances these processes have been successful they are for the most part still in the experimental stage.

Textile Printing. Textile printing differs from dyeing in that the color or colors applied are confined to certain portions of the material, thus producing definite designs or patterns. The chief object of textile printing is the production of a pattern fabric in colors at a low cost, the duplication of which by weaving would be excessively expensive or impracticable for some other reason.

In cotton printing, perfectly plain cotton cloth commonly known as print cloth or calico is used, and the patterns produced are wholly inde-

[1] Beams are the large tightly rolled cylinders of warp which are placed in the back of a loom.

[2] Cops are small conically wound portions of yarn which are placed in the shuttles of a loom.

pendent of the weave. There, are, however, what might be termed fancy-prints, where the finished design or effect is produced partly in the loom and partly in the printing machine, and other cases by the combined effect of printing and mercerizing, or printing and embossing. Only one side of the cloth is usually printed, but occasionally both sides are printed, either by passing through two different machines, or a special machine arranged so as to print both sides at the same time.

The textile printing process proper is of a mechanical nature, but the preparation of the various printing pastes or colors, as they are called in the works, the methods of applying them and their actual fixation upon the fiber involve a greater number of chemical principles and a greater variety of dyestuffs and chemicals than any other branch of textile coloring.

Cylinder or Roller Printing. At the present time the cylinder or roll printing machine, which originated in England during the latter part of the 18th Century, is used almost exclusively for textile printing. Although its mechanism has been greatly improved and its range of possibilities wonderfully extended since its introduction, the principle involved remains the same, namely: the passing of the cloth which is to be printed, under some tension, and very great pressure between an engraved (intaglio) metal roll (usually copper), the engraving of which is filled with color paste, and a large cylinder which is well padded with an elastic covering.

Printing Proper and Application of Color. The modern textile printing machine, especially one intended for printing a number of different colors at the same time, is complicated and can only be properly handled by one who is acquainted with all its parts and who has had long experience in its use.

To give anything like a complete description of the intricacies of such a printing machine, or discuss the many precautions and rules which must be followed in its use is beyond the purpose of the present consideration. An attempt will, however, be made to explain the principles involved in its use.

Brief Description of Printing Process. By studying Fig. 361, which represents a one-color machine in cross-section, the general principles of textile printing by means of the roller printing machine will be apparent:

E R represents the engraved printing roll which bears (sunken below the surface) the design to be printed.

C B represents the color box, pan or trough which holds the color paste that is to be printed upon the cloth.

F represents the color furnisher, which consists of a revolving cylindrical brush or felt covered roll, half of which is immersed in the color paste. It revolves parallel to the printing roll with which it is brought in contact under sufficient pressure to completely fill the engraving of the roller with the color paste.

The printing roll revolves in the direction indicated by the arrow

head and the excess of color is removed, and the unengraved portion of the roller scraped perfectly clean by the color doctor *C D* which consists of a metal blade (usually steel) with a very accurately ground edge.

The printing is accomplished at the nip (*N*) between the printing roll and the pressure bowl or roll *P B*. This pressure roll consists of a large cylinder covered with a number of thicknesses of so-called lapping which furnishes an elastic and springy back for the cloth that is being printed. The pressure between the printing roll and the pressure roll is so great that the cloth to be printed is practically forced into the depths of the

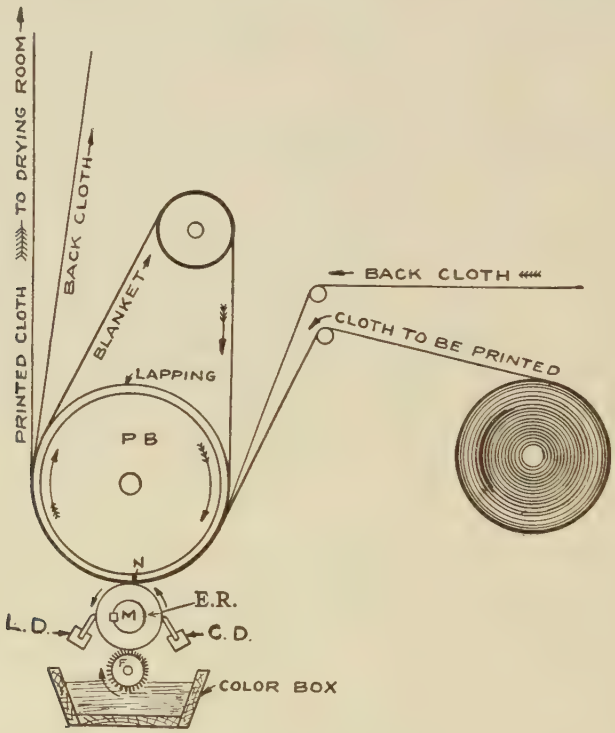

Fig. 361.

engraving by the expansive force of the lapping, as well as of the blanket and back cloth which are always run between the cloth and the pressure roll. The color is thus extracted by the cloth from the engraved portion of the roll, while that portion of the cloth coming in contact with the unengraved portion of the roll, from which the color has been removed by the color doctor, remains unprinted.

The lint doctor *L D* is similar in construction to the color doctor but is located upon the opposite side of the print roll. Its object is to remove lint and threads as well as any particles of partially dried color paste which might be carried into the color box.

After leaving the printing machine the printed cloth is passed as quickly as possible to the dryer.

Styles of Printing. When the term style is used in relation to textile printing the term refers to the chemist's or colorist's part of the work, rather than the artistic or mechanical. The designer and engraver may determine the exact detail of the design, and perhaps the color combinations desired, but it still remains for the chemist or colorist to determine just how such colors and desired effects can be produced upon the cloth, and it is the particular operation or series of operations producing the effect which the printer designs as style.

There are a dozen or more different styles used in textile printing of which the following are among the more important:

1. Direct printing style.
2. Pigment style.
3. Steam style with tannic mordant.
4. Steam style with metallic mordant.
5. Madder or dyed style.
6. Ingrain or developed azo style.
7. Discharged dyed style.
8. Discharged mordanted style.
9. Resist style.

Style I. Direct Printing. The term direct printing style has been used differently as well as vaguely by various authorities on printing. Some include the printing of pigment and basic colors, as well as mordant colors under this heading, and as a matter of fact it might rightly be said that every printing process involved direct printing.

To avoid confusion, however, and to make our classification of styles as complete and concise as possible, we shall designate as direct printing only the printing with such dyestuffs as have a direct or self affinity for the fiber without undergoing any chemical change or requiring any special solvent or reducing agent as is the case with the sulphur colors and indigo and its derivatives.

The direct printing style from this point of view includes only the printing or direct cotton colors, upon vegetable fibers and direct cotton, basic, phthalic anhydride and acid colors upon wool and silk.

The dyestuff is prepared with the necessary thickeners and sometimes with the addition of certain assistants which aid in the penetration and fixation of the dyes. Very little direct printing is done upon cotton, as the only dyestuffs at all suitable are the direct cotton colors, and they cannot be used to any extent on account of their property of bleeding.

With wool and silk direct printing is depended upon very largely.

Style II. Pigment Style. This consists in printing directly upon the material some pigment in a very finely divided condition in conjunction with some adhesive substance which will hold it fast to the fiber. Albumen

is commonly used for an adhesive as its property of coagulating renders it especially suitable for the purpose. It is readily soluble in water at ordinary temperatures and can be uniformly incorporated into a printing paste with the desired pigment and the necessary thickeners. After printing, the cloth is subjected to a steaming process during which the albumen coagulates to a very insoluble form which firmly holds the pigment upon the fiber.

Style III. Steam Style. Tannin Mordant. This consists in printing upon the material a color paste containing a basic dyestuff, tannic acid, and some volatile acid, usually acetic, but less frequently formic acid, together with a small amount of some non-volatile organic acid, usually tartaric.

After printing the cloth is steamed and then passed through a solution of some antimony compound, containing chalk in suspension, which completes the fixation of the color. The whole process is followed by a thorough soaping.

Style IV. Steam Style. Metallic Mordant. This style is produced by using a printing paste which contains a mordant color, some metallic mordanting principle, usually a small amount of some organic acid, and the proper thickeners. The mordanting principle used must be of such a character as to readily undergo decomposition during the steaming process which follows the printing, thus producing a metallic mordant which will unite with the mordant color and produce an insoluble color lake.

Style V. The Madder or Dyed Style. The madder or dyed style is produced by first printing upon the material some metallic mordanting principle which will readily liberate the actual mordant when the cloth is subsequently aged or steamed. The fixation of the mordant is completed by a dunging process.[1] The cloth thus printed and prepared is dyed with a mordant color which unites with the mordant already present, producing a definite pattern.

Style VI. Ingrain or Developed Azo Style. With this style no actual dyestuff is used in any portion of the process, but the final result is the development of an insoluble azo color upon the fiber.

Two reds, para red, a bright red similar to Turkey red; and alpha-naphthylamine red, a claret color; are used almost exclusively for this style. The former by printing diazotized para-nitraniline and the latter diazotized alpha-naphthylamine upon cloth previously prepared with beta-naphthol.

Style VII. Discharged Dyed Style. In the production of the discharged dyed style the material is first dyed all over usually by the padding process, or in the jig dyeing machine and less frequently in the ordinary string dyeing machine. Upon the cloth thus dyed there is printed the so-called discharge which is a printing paste carrying some substance

[1] The modern dunging process consists in passing the cloth through a bath containing such alkaline fixing agents as chalk, sodium phosphate and silicate.

capable of completely destroying or decolorizing the dyestuff already present.

A perfectly colorless figure may thus be produced upon a colored ground, or it is possible to introduce into the discharging paste some dyestuff which is not affected by the decolorizing agent, thus producing a colored figure upon a different colored ground.

Style VIII. Discharged Mordant Style. This consists in first mordanting the cloth, then discharging the mordant by printing upon it the proper discharge, and subsequently dyeing. There are two quite different types of this style, one in which a tannin mordant is discharged by printing on a caustic soda paste and steaming, the material then being dyed with a basic color and another in which a metallic mordant is discharged by printing on some organic acid, aging and then dyeing with a mordant color.

Style IX. Resist Style. As with the discharge style the object of the resist style is to produce a white or colored pattern upon a different colored ground. The appearance of the two styles may be identical in some instances and the chemistry involved in their production may be the same. The difference between the two lies in the fact that the color destroying agent is first printed upon the cloth and when the dyestuff is subsequently applied absorption and fixation of color is prevented upon the printed portions. Colored resists may be produced by introducing into the printing paste a color not affected by the resisting agent.

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CHAPTER XLIV

THE PAPER INDUSTRY

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Historical. The making of paper is one of the oldest of the arts. There has been found rolls of papyrus made, about 6000 years ago, by the ancient Egyptians out of the papyrus plant, a reed that grows to-day, wild, along the banks of the Nile. The Chinese, from whom the Europeans received their early instruction in the art, made paper from the inner bark of the mulberry tree upon which they made records of incidents that they desired to preserve for posterity.

Parchment made of the skins of animals was also used for many years for records. Erasures of old records were common, so that the parchment might be used again in order to save the cost of buying it anew. The chemist, in a number of instances, has reproduced successfully these older records thus bringing to light some very valuable writings. Probably on account of the ease of making, using, carrying and handling these parchment rolls they came into general use.

Until about the year 1800, paper was made out of cotton and linen rags, using the crudest of machinery and producing what is called "hand-made paper." Awakening along inventive lines in this art seems to have started somewhat before that time, as we have accounts published in 1765, suggesting the making of vegetable tissue into pulp and bleaching it into paper stock. Straw, wood, bark, hornet's nests, hopvines, cabbage-stumps, thistle stalks, burdock, and peat were all mentioned as suitable material for this purpose.

To-day for raw stock we use cotton and linen rags, wood fibers, straws, old ropes, jute, etc., to a limited extent. Many other vegetable fibers are also used. The varieties of paper and allied products are too numerous to attempt to describe individually in a small chapter. Determination of the different fibers is accomplished by aid of the microscope and the chemical reagents which are described by Cross and Bevan, Herzberg, Höhnel as well as other authors and investigators. In general, each fiber has some peculiarity of construction or reaction by which it can be separated and accurately determined. Exhaustive work in microphotography has

furnished excellent descriptions that can be easily followed in making examinations of unknown fibers.

Raw Material. At the present time the manufacture of paper has two principal bases of supply. One of these is cotton and linen, the other is wood. Out of rags is made the highest grades of paper.

Immense quantities of wood is made into paper by grinding (see Mechanical Process) and by chemical treatment (see Soda Process, Sulphite process, Sulphate Process). Straws of different kinds as rye, wheat, rice, yielding a short, weak fiber, and flax, yielding a long strong fiber, are converted into paper stock by chemical processes, generally a modification of the caustic soda treatment. Jute, hemp, manila (one of the strongest fibers), sisal, New Zealand tow, esparto and similar fibers are also generally cooked in rotary digesters under the caustic soda treatment, as are cotton-seed hull linters, cotton stalks, corn stalks (giving interesting by-products of cattle food)—and many others when they can be made to yield a fiber at a profit.

Rag Paper. All linen and cotton rags can be converted into different grades of paper according to the kind and color of the rags. Great care is used in sorting rags before delivery to the paper mill so as to get a uniform kind of rags of the same color. Buttons, pieces of metal, sticks, stones, rubber and all foreign articles, must be removed.

The treatment of rags in the mill is as follows: The rags are delivered at the mill in strap iron bound bales about 3 ft. square and 5 ft. long. Often several hundred tons and sometimes two or three thousand tons are kept on hand.

The rags in bales as demanded for use, are taken to the ragroom where the bales are opened by women who make the final sorting, inspection and cutting. The finest sort goes into the best of writing paper. From this high standard to the pasteboard and cheapest wrappers are many grades supplied by the different quality of rags.

A scythe shaped knife is fastened in a vertical position to a table by which the operator cuts the rags fine or coarse, and also separates out all foreign matter that may be seen. At this stage the rags pass to the mechanical rag cutters that cut them up into small pieces so that the *Duster* through which they next pass can remove much of the loose dirt. These machines dust out oftentimes five per cent or more of the weight of the rags and also open them up so that the chemicals, milk of lime or soda ash, in the *rotaries* or cookers into which they next are placed can better penetrate and act upon them.

Rag Boilers. Rag boilers are of several types. The stationary upright cylinders are provided with a manhole on top for filling, the cover to which is bolted on or held up by yoke and bolts. By the opening of a valve, at the bottom, the contents are blown out, due to the pressure (generally about 30 to 50 lbs.) maintained for six to eight hours during the cooking. Steam for cooking is admitted at the bottom and the

liquor circulated by an outside pump or by an injector inside the digester.

Rotaries are horizontal cylindrical-shaped steel tanks 10 to 20 feet long and 6 to 8 feet in diameter with heads riveted on each end, each head having a journal upon which it rests and is turned during the cooking process. Hence the name " Rotary." Through one of these journals steam enters for cooking. The rotary may have one or two manholes with covers affixed, as in the upright, for filling in the stock. During the filling men go into the " Rotaries " and pack the stock into the ends so as to get in enough to properly fill the boiler.

Rag Boiling. The chemicals, a certain number of gallons of a solution of caustic soda or soda ash and caustic lime, or a milk of lime made by slacking and boiling caustic lime in water are added. In all cases where lime is used it should be strained in order to remove unslacked parts before being passed into the cooker. When the liquor is all in, the covers are adjusted and the steam turned on. The pressure generated (generally 15 to 30 lbs. to 50 lbs.) and the chemicals reduce the foreign matters, such as grease, loading materials, dirt, etc., and open up the fibers so that in the next operation of beating they can be perfectly cleaned and reduced to the desired length. Some manufacturers blow off the cooking liquor of the rotaries and run in fresh water to wash the stock in the rotaries, but generally the stock is dumped as soon as cooked and pressure lowered by removing the covers of the manholes. Sometimes the stock is allowed to stay in piles for several days in order to ripen after it is cooked. It is eventually taken to the beater engine.

Beater Engine. This is a Holland invention, sometimes called a Hollander, for washing, beating and reducing the fibers of the paper stock made in various shapes and sizes. The following is a general description of a type: The beater engine is an oval-shaped tub about 20 feet long by about 3 feet high by about 8 feet wide. It is made of wood or iron shell with floor of wood or cement and is often lined throughout with copper. A partition, the " Midfeather," extends as far as the rectangular part of the body. A beater roll 4 to 5 feet in diameter with heavy knives parallel to the shaft is fitted into its face and is suspended in one of the divisions nearly filling it. This roll can be raised or lowered, by the beater man, nearly onto the bedplate, which is a number of steel plates standing on edges bolted together. The raising or lowering of the roll determines the ultimate length, and in a great measure the condition of the fiber when finished. Between the roll and the bed plate all of the stock must pass. The circulation of the stock around the beater is given by the roll which acts as a paddle wheel. While the stock is washing, clean water is added at one side of the roll. This is thoroughly mixed with the stock as it passes under the roll and on the other side a revolving drum washer with a fine wire on its face is pressed into the pulp. The dirty water is thereby removed from the stock.

This process is continued until the stock is clean, during which time there is but little cutting done by the roll or bed-plate (as the roll is raised). At this point the stock is often bleached in the beater by means of a solution of calcium hypochlorate, generally called bleach. This bleach is made by mixing common bleaching powder with water preferably in concrete tanks, in a series of three or four, in order that the bleach may be made, settled, and the sludges washed to a final test of about $\frac{1}{2}$° Bé. when it (the sludge) can be thrown away; using the clear washing liquors to build up or to mix the bleaching liquor for the right test. Only a clear bleach solution, testing about 4° to 5° Bé., should be used. Heating the stock carefully is frequently done, to hasten the bleaching, especially in the continuous bleaching systems. It demands close attention to prevent burning and rotting the stock. Only a clear bleach solution, testing about 4 to 5° Bé., should be used. When bleached to the requisite color the stock is either dumped to a drainer to finish the bleaching or to be thoroughly washed; or it is washed in the beater by the addition of more water and often some antichlor is added to hasten the *killing* of the bleach. Washing is kept up until these chemicals are washed out, then the roll is gradually lowered and the pulp is reduced to the proper condition. When nearly "*ready*" the required color, if any, is put into the beater, then size, if it is to be engine sized, is added. The size is made with soda ash about one part, rosin about four parts, dissolved and thoroughly boiled in water, well diluted, and then alum introduced to set the sizing onto the fibers. The stock is run in the beaters a short time and then dropped into the stuff chest, where it is kept well stirred until it is wanted on the paper machine.

Jordan Engine. In its passage to the machine the stock is generally run through a Jordan engine that reduces its fibers to final readiness for the sheet of paper. This engine is a cone-shaped plug, about 4 feet long, made up of steel bars and hard wood, that fits into an iron sleeve or hollow cone made to receive it, being lined with a filling similar to that on the plug. Through this Jordan all the stock passes and by the closeness of the plug to the sleeve the stock is finally reduced to the proper condition for the machine, It is then sent to the *machine stuff-chest* from which it is pumped to the *flow box* where the right quantity of water is added to make it flow properly through the *screens*. The screens remove all particles too coarse to go into a sheet of paper. The stock passing through the slots, which are generally about $\frac{1}{100}$ of an inch in width, drop to the apron and then onto the wire of the machine, if it is a Fourdrinier.

Robert Patent. In about the year 1799 Robert took out a patent in France on a machine making endless paper. Not being successful, there he associated with him in London Fourdrinier. They spent $300,000, which at that time meant more than it does now, in their endeavors to put into general use their machine. They were never financially rewarded,

but their machine, "The Fourdrinier," revolutionized paper making, creating a foundation upon which has been built the ninth largest industry of the United States to-day.

Fourdrinier Machine. Paper may be made on the Fourdrinier type with a wire at the wet end upon which to form the sheet; the Harper type with felt and wire, or the cylinder machines. The difference being principally at the wet end, where the paper is formed. The drying ends are as a rule similar. The cylinder machines have from one to six vats with cylinders in each, making a sheet of paper that is laid on the next in front so that when finally they go to the felt it is a built-up sheet of one, two or more sheets of paper according to the number of vats used to make it. When dry the whole sheet can be split up into the different sheets it is made out of. Much of the heaviest paper is made on this machine, which, however, is not a fast running one.

The paper machine in general use for news and many other kinds of paper as well as rag is the "Fourdrinier," which, while it does not make as thick a sheet as the others, can make light as well as medium weights easier, change quicker, run faster and produce a good tonnage.

The wire of the Fourdrinier machine is made endless, i.e., its ends are woven together so that it will pass around the rolls like an endless belt and it is stretched out like a horizontal oblong table. It is supported by a series of brass rolls at intervals, as demanded by the work to be done. Its width varies from 36 to 200 inches, the length varying in due proportion. A rubber deckel strap about 2 inches square runs at each side to hold the pulp and water on the wire, also by the moving in or out of the deckel straps, the width of the sheet can be changed to meet the demand. The proportions of these parts are such that the sheet of paper can remain on the wire long enough to get rid of its superfluous water by draining through the wire, by squeezing out water in passing between presses, couch rolls, over suction boxes, etc.

This wire is one of the most important and costly parts of the machine. Its condition means the appearance of the sheet of paper. Great care is taken to keep knots of stock, stray pieces of iron or wood or any hard foreign matter, off the wire as a puncture, a tear, or any damage to it means a shut down of the machine until it is made as nearly perfect as possible. The wire must be kept clean so that the water can freely pass through it anywhere. Should it plug up, the stock is shut off and the plugs cleaned off, as a thin spot in the sheet of paper would show each time the spotted section carried the sheet along. The sewing of the wire is a delicate piece of work and must be done so as to match the weave of the wire, and not leave a mark on the sheet of paper. The sheet of paper is fully formed on the wire. While in the forming state the fibers of the sheet are felted together by the shaking motion, which, although a very short stroke, in itself seems to make a felting of fibers that distinguish a tough Fourdrinier made sheet from a cylinder made sheet, wherein the fibers all

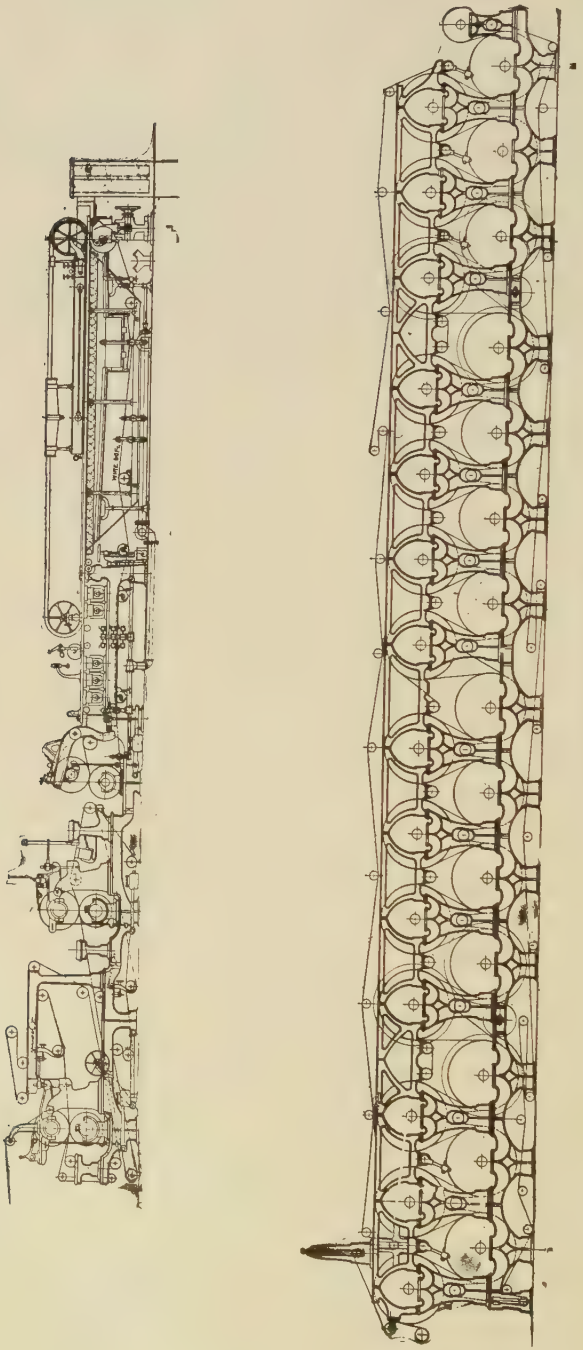

FIG. 362.—Fourdrinier.

run in about the same direction. There is also often a dandy roll that places a name or figure in the paper, such as one can see when it is held up to the light. This stamps the name into the sheet of paper while it is wet and is sometimes called a " watermark." With all this manipulation two-thirds of the weight of the sheet of paper before going to the steam dryers is water.

At the end of the wet end nearest the dryers is the last press through which the wire passes. The sheet of paper will now be well formed and leave the wire and stick to the surface of the top roll. A sharp-edged scraper, called a doctor, prevents the sheet from passing entirely around the press. At this point the back tender strips off the roll a 2- or 4-inch wide piece and carries it across the gap to the first dryer. As the speed of the machine is from 60 to 600 feet a minute for this sheet of paper much dexterity is required at this place. A man stands at the press roll, gradually working the strip that he started tearing off at the end of the press, across to the other end, making a diagonally cut sheet that eventually grows from the 2-inch wide strip to one the full width of the sheet of paper.

The *dryers* are steam heated hollow cast iron cylinders 3 or 4 feet or more in diameter with a width of from 36 to 200 inches as the machine

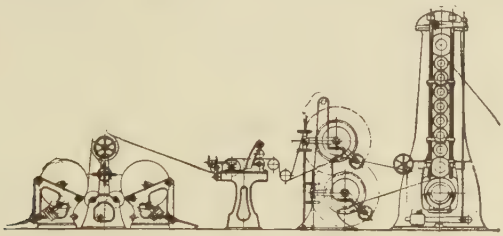

Fig. 363.—Calenders

may be built, placed one above the other as shown in Fig. 362. A strong cotton duck dryer felt is held up to the bottom dryers by rollers in order to hold the wet sheet up to the hot surface. The sheet of paper goes about two-thirds around the bottom dryer, up and over to the top dryer where it comes into contact with as much of that surface as it can and drops down to the second bottom dryer. This is repeated until it has come into contact with all of the dryers of the machine (ten or sixty, according to the make), when it leaves the machine and is passed by hand to the reel or up to the top pair and down between the others of a stack of calender rolls between which it is run to smooth or polish the surface of the sheet. From the calender (Fig. 363) it passes to the reels; from the reels through the slitters that cut the sheet into the width desired and then to the winders where it is wound up into rolls. When demanded these rolls are taken to an apparatus called a super-calender, where the surface of the sheet is further polished by running between

heavy steel rolls, and then it goes to the *cutters*, where it is cut up into any size of sheets demanded. From the cutters it goes to the counters. These, who are generally girls, count out the sheets into 12, 24 or 500 sheets ready for the finisher and packers who make up the packages of paper as they are ordered for the trade.

Wood Paper. Wood paper is made principally from logs from the woods where the trees are felled and cut up. They are either floated by river or taken by railroad to the mill if to be converted into paper. Many mills are located contiguous to a saw mill in order to use the waste therefrom to help out the supply of wood. From the different varieties of spruce, pine, fir, hemlock, poplar, and other woods, we obtain practically all of our newspaper, nearly all even of our book paper, and a large portion of our writing papers.

On the arrival of the wood at the mill, if it is to be chemically treated, it is generally piled up so that it may dry; it is allowed to thus season in the pile for one, two or perhaps three years. This seasoned wood loses much of its sap and water and requires less chemicals to convert it than the green wood directly from the forest. For the mechanical pulp a fresh green wood produces better fiber and is easier ground up than the dry seasoned wood. For any of the treatments the bark must be removed, which is done by a machine called a *barker* or by the hand draw-shave.

In the wood paper industry the principal methods of treating wood to produce fiber are by grinding, producing ground wood or mechanical fiber, and cooking by either the caustic soda, the sulphite or the sulphate process.

Mechanical Process. The mechanical process consists of placing blocks of wood about 18 inches long in apertures, called pockets, of a heavy cast-iron frame that encases a large grindstone. This grindstone revolves at about 200 revolutions per minute, a stream of water plays against its face to keep the wood from burning, as it is pressed against the face by hydraulic pressure of about 30 pounds. The result of this is the reduction of the wood to a fine pulpy mass, which is called mechanical pulp or ground wood. This is floated by water on to a coarse screen by which the pieces of wood that have not been ground up are removed. The pulp goes to a fine screen through which the mechanical pulp, that is, the right kind to go into the making of newspaper or other papers, passes. This pulp now goes to the beaters in the beater room to be mixed with sulphite pulp or other stock, according to the grade of paper it is desired to manufacture, and from the beaters goes to the paper machine, as described under Rag Paper, or to a wet machine, which is an apparatus for getting the pulp into a state dry enough to handle. The *Wet Machine* is a wooden vat 6 feet wide, 8 feet long and 5 feet deep, into which the mixture of water and ground wood is pumped. A bronze cylinder about 3 feet in diameter by 6 feet long, covered with a brass wire net of 60-mesh, is immersed in the mixture in such a manner that the water passes through the meshes

of the wire, leaving the pulp sticking to its surface. A coarse woolen blanket called a felt, is pressed against the cylinder mold by a heavy couch roll. The blanket automatically picks off the pulp from the face of the cylinder, carries it along on its surface over a suction box and between heavy press rolls that extract quantities of water from it and leave it with from 35 to 50 per cent of pulp. One of the rolls of the press is of hard maple wood which picks the pulp from the blanket when it comes it contact with it. As the press roll revolves the pulp is continuously added to it from the blanket until the sheet is thick enough in the judgment of the press tender, who then with a sharp pointed wooden pin cuts it off by passing the point under the sheet close to the wood roll, across the face of the roll. The sheet of pulp is rolled off on a table folded up, weighed and is then ready for shipment or storage.

Chemical Pulp is made by treatment with either caustic soda, bisulphite liquors, or sulphate liquors. Soda fiber is made by treating poplar and similar wood with caustic soda in digesters, which are large steel boilers. This process was put into practical use in 1875.

Soda Process. The caustic soda liquors are made in the paper mills using this method by dissolving soda ash in water, and to this solution adding about 55 to 60 per cent of freshly burnt pure quicklime, bringing the mass to a boil, mixing it thoroughly by stirring, then allowing the calcium carbonate, which is produced by the reaction with the soda ash, to settle to the bottom. The clear caustic liquor is siphoned off, the lime sludge is washed two or three times with water to remove as much of the caustic soda as possible. Attempts have been made to reclaim this lime sludge by drying it and reburning it, but this is seldom done.

Poplar wood and kindred species are principally used in the soda process, as they yield easiest to this treatment, requiring a smaller amount of caustic soda for reduction than do other woods. The well-seasoned wood from the piles, where it has lain for a year or more, is brought to the mill where it is inspected and all bark, dirt and black knots removed, as these make objectionable color and dirt in the pulp and paper. These sticks of wood are then taken to a machine called a *chipper*, which slices off the wood into slices similar to a sliced onion that break into chips about $\frac{7}{8}$ inch long by 1 inch by $\frac{1}{4}$ inches. The thickness of these chips will generally be the annual growth of the wood. The chips are screened to remove the sawdust, knots and coarse pieces. These coarse pieces, passing through a re-chipper, are reduced to the proper sizes. As the sawdust produces a fiber which is too short for use and if allowed to remain mixed with the wood would consume a proportionate amount of chemicals, it is carefully screened out and is used for fuel. Many experiments have been tried for the utilization of sawdust for fiber but none have proved successful. The chips are stored in large bins by conveyors placed over the digesters into which they are run through spouts by gravity. These *digesters* for the soda process are made of steel 1 inch thick and are

sometimes 50 feet high and 10 feet in diameter. They are filled full of chips and then is added a certain amount of the caustic soda solution of a density of 8 to 10° Bé., according to the character of the wood to be cooked. When filled, the cover of the digester is bolted down and steam is turned on through the bottom. In the soda digesters there is a false bottom which allows the hot liquor to pass down through it. There is generally an ejector under this false bottom through which ejector steam is passed which lifts the cooking liquor at the bottom, carries it through a pipe to the top of the digester and sprinkles it over the chips, thus making a continuous circulation which produces thorough cooking. The cooking of the chips dissolves everything but the cellulose, the fibers. When completely cooked, the contents of the digester will be found to have shrunk one-quarter to a third of its bulk, but the chips retain their original form at this point.

A cooking pressure of 90 pounds is maintained in the digesters for from eight to ten hours with frequent opening of the relief valve at the top to draw off gas. A sample of pulp is drawn to ascertain if the wood is properly cooked. When the operation is completed a valve of 6 or 8 inches diameter at the lower part of the digesters is opened and the entire mass is violently blown out of the digester by pressure into a suitable receiving tank. This violent action and the impact of its contents serves to shatter or destroy the original form of the chips and a pulpy mass of fiber results. The liquor which has been employed for the reduction, now called black liquor, is carefully drawn off, by repeated washing with weaker liquors or water in the wash tanks, evaporated to a consistence of 35 to 40° Bé. by means of some suitable multiple-effect evaporator. It goes now to a rotary furnace, where it is further dried and the tar and other wood products are burned up, leaving the soda mixed with charcoal. This black mass is called "black ash," and is put into the tank. The soda which it contains is leeched out and is used over again with addition of fresh soda ash and caustic lime. A recovery of from 85 to 90 per cent of the original soda ash used is generally obtained and this materially reduces the cost of chemicals employed. The profits of the mill are largely dependent upon this part of the manufacture. All soda fibers, when cooked and washed clean from the cooking liquors, are somewhat colored and if a white paper is desired they must be bleached to the desired whiteness. If a colored paper is demanded, the color desired can be made in many cases without recourse to bleaching. The pulp, when washed clean, is passed through screens which remove from it uncooked wood and coarse matters and either goes to the beaters where it is mixed with other fibers in the beaters to make the desired grade of paper or it is bleached, if required, and then pumped to the wet machines previously described, to put into condition for handling in shipment or storage. Soda fiber is a soft stock and is largely used in the better magazine, book and writing paper grades. It is of a soft, spongy-like feeling to the fingers and is

a quality desired in paper used for books. It is a fiber that does not deteriorate by time as the chemicals that have produced it do not have a rotting effect upon it unless it is overbleached. Its selling price when bleached is $45 and up per ton.

Sulphite Process. Sulphite fiber, perfected in 1885, is made by treating spruce and similar woods with sulphurous acid, combined with lime and magnesia, in special digesters made by lining to withstand the action of the corrosive acids. The largest amounts of chemical fiber is produced by this process. The spruce, fir and hemlock from which most of this pulp is made is piled, dried, cleaned, chipped and screened and conveyed into the chip bins above the digesters practically in the same manner as for the soda process. The digesters for this process are built of heavy 1-inch steel and are very large, being often 50 feet high by 18 feet in diameter made to contain 20 to 30 cords of wood at a charge.

On the inside of these digesters there is generally placed a protective lining of lead fastened to the shell of the digester or a backing of about 6 inches of Portland cement plastered onto every part of the inside steel sheel of the digester, then up against this cement is laid an inside facing of vitrified acid proof or other brick laid up in a cement made of Portland cement, litharge and glycerine, because the acid, if it comes in contact with the steel, would attack it. Great care is used in protecting the inside shell, and in properly conducted mills examinations are made of it after each blow to see that no injury is taking place to the lining.

These digesters are loaded full to the top with chips and bisulphite liquors run into the digester to within about 3 feet of the top. The bisulphate or cooking acid is made by burning in specially built furnaces. In some of the countries of Europe pyrites, on account of its cheapness, is used instead of the sulphur, but it has not been found profitable to use pyrites in this country. The greater part of the sulphur used in this country comes from the underground sulphur mines of Louisiana, where it is obtained by forcing superheated steam down a pipe which melts the sulphur and forces it up the casing as a brown liquid. The melted sulphur is run off into piles where, when cool it returns to its yellow sulphur color. Louisiana sulphur has practically driven out of the market, in this country, the Sicilian sulphur formerly used. When the Louisiana sulphur came into use much trouble was caused by the impurities that it contained which would form a coating over the molten surface and prevent the formation of the sulphur dioxide gas. This difficulty is now overcome by the invention of rotary and agitating burners. The gas is generated by burning sulphur in the furnace admitting the right amount of air so that the chemical combination of two atoms of oxygen with one of sulphur may take place. To further insure a combustion a chamber is attached back of the furnace where a further supply of air is carefully admitted bringing the sulphur dioxide gas to 14 to 18 per cent. The gas first goes through cast iron pipes to cool it, then it enters lead

pipes immersed in cold water to further reduce the temperature. It next passes successively through three or four wooden tanks containing milk of lime to absorb the gas. The milk of lime best suited for this purpose is made from dolomite often carrying 45 per cent of magnesia. The gas enters the tank at the bottom, leaves at the top and then mixing with the milk of lime in successive tanks till the sulphur dioxide is all absorbed and the residual air passes out of the heavy vacuum pumps that pull the gas from the furnace to them. Or the gas may be absorbed by the tower system, when it is passed into towers about 100 feet high, where it comes in contact with limestone and water and by its acid action on the lime rock produces the liquor necessary for the reduction or cooking of the wood. The strength of the acid is tested by iodine solution, using starch as indicator and is generally run at a Bé. strength of 4 to 6° containing the proper amounts of free acid and combined acid according to the wood that is to be cooked.

The digester having its complement of acid is sealed and relief pipes connected to the top cover. The digester has no false bottom and the steam is applied directly through its cone-shaped base. The circulation of the digester depends on the passage of the steam into the bottom, working its way up through the mass of chips and liquor, causing the sulphur dioxide to break loose from its combination with the lime and magnesia, the resultant gas being relieved through the escape valves on the top of the cover. This gas, as well as the liquor that is blown out through the relief pipes, is valuable up to two-thirds or more of the time of the cooking. They are cooled by running them through lead pipes immersed in cold water and are mixed with fresh cooking liquors. This is the only method in use at present of reclaiming the sulphur. There has not thus far been invented any system of circulation for the sulphite cooking such as is in use in the vertical soda digesters. Both the soda and sulphite processes have digesters or cookers that are placed horizontally and are rotated, but they are not used as much as the vertical or upright digester on account of the extra labor required to fill and to dump them. The vertical digesters are self emptying, thus lessening the cost of labor and time.

In the cooking of the sulphite pulp in the digester the mass of chips shrinks as in the soda process. During the process a pressure of 90 pounds is maintained in the digester and the temperatures run as high as 350° F. The quick cooks are made in six to ten hours, the slow cooks are steamed from thirty-six to seventy-two hours. The slow cook produces the strongest fibers that we have and uses a weaker strength of chemicals than the quick cooks. The vertical digesters are discharged in a similar manner to the soda ones. The pulp on being blown out strikes a bronze plate called a *target* and is almost white. The cooking liquor is at once washed out of the pulp by flooding the tank, into which it is blown, with fresh clean water. The tank has a perforated bot-

tom connected to the sewer, with a valve so as to control it easily. The water used for the washing, strange to say, must be pure and more care taken to insure its cleanliness than with the water we generally drink. This waste liquor has been experimented on extensively, but up to the present time it is found to be of value only in tanning and as a binder for slack coal in making briquets for fuel. The cooking acid must be thoroughly washed out of the sulphite pulp, because if it is not the color of the pulp, it will turn pink or darken to a light-gray slate color. After washing the stock is passed through screens with mesh not finer than $\frac{1}{10}$ inch, through which the fiber itself passes, leaving behind the knots and uncooked pieces and coarse stuff, which are sent to the scrap heap to be ground up. When sulphite pulp is to be shipped to another mill or piled up and stored it is run over the *wet machine* which has been previously described. If there is a newspaper mill connected with the plant, the ground wood and the sulphite are each pumped to it and mixed together in beater engines. For the common newspapers 75 per cent of ground wood pulp is mixed with about 25 per cent of sulphite pulp, some size and alum is added and a little pink and blue aniline to give it the required white tint. After beating in the engine from a quarter to a half hour, the stock is dropped into a stock chest, whence it is pumped to a Jordan engine, which shortens the fiber to the proper length for the sheet of paper. From the Jordan engine it goes to the stock chest that supplies the paper machine, being the same type as the one described to make rag and writing paper, only it is much heavier, costlier and runs faster. Some of these machines cost as much as $80,000 each and are marvels of beautifully adjusted mechanism. The different parts are so accurately adjusted that from the flow of the wet stock onto the wire to the winding up of the dried sheet of paper as it comes through the calenders it moves with perfect adjustment whether the speed be 300 or 650 feet or more per minute.

The Sulphate Process, Kraft-paper. With some modifications this process is similar to the " caustic soda process." The Dahl patents issued in 1884 cover much of the process as is in practice to-day. The liquors are made caustic by the addition of freshly burnt lime, the waste of the soda is made up by the addition of salt cake. The percentages of the chemicals must be accurately determined, generally keeping about seven parts of caustic soda to four parts of sodium sulphate.

Woods that hardly yield to the other processes are easily converted into sulphate or Kraft. Most of the conifers, and some of the other woods, are treated successfully. The resultant fiber is much the strongest of the wood fibers and is seldom if ever bleached.

The yield of fiber is high. The recovery of the liquors is the hardest part of the process and special incinerators have had to be devised to help the conversion back to the carbonate.

There are very few mills making Kraft in this country and they are

generally placed in thinly settled sections because the waste gases are very offensive.

Paper from Waste Paper. This has recently become a big industry in itself. Many of the cities have paper waste gatherers who pick up, sort over, and bale up tons of paper daily, all of which goes back to the paper mill to be made over into some form of paper, wrapping, sheathing or boards. There are several types of shredders as well as cookers and washers. When a light-colored paper is desired the use of chemicals becomes necessary. For boards the papers are fed into the beater engines and beaten up, washed, steamed, and when in fine enough condition, are ready for the machines.

Wastes. The paper mills in this country will eventually be compelled to return the water as clean as received. State legislation is now compelling the separation from the waste waters of the clays, fibers and water by the use of sedimentation tanks. Also filter beds of sand and cinder covering acres of land are used to separate the sludge from the more or less clean water that must be run into the river.

Although great improvements have been made in the many types of save-alls that are in use for saving fibers, clays and other paper stock there is still room for better apparatus. Careful attention to this subject should well repay any paper-maker as well as decrease the river pollution nuisance.

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CHAPTER XLV

CELLULOSE INDUSTRIES

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An interesting feature of the Cellulose Industry, in the narrow sense of the term, is that in every case the industrial developments have followed research work in a chemical laboratory. It is not the case, as in so many other industries, that an article was produced on a manufacturing scale and perfected or developed further by laboratory work, but rather that the laboratory work is here in every case the pioneer. It is important, therefore, to base our considerations of these industries on a careful study of the properties and reactions of cellulose. These reactions are studied in regard to their technical significance in the first part of the chapter while the operations on the manufacturing scale are discussed in the latter part.

Definition. Cellulose is the structural material of vegetation, the substance of which the walls of plant-cells are composed. Just as a chemical reaction is conducted in a container of resistant material such as glass, so the vital processes of the vegetable cell are carried on inside its envelope of cellulose. The union of a number of cells produces a fiber, and the fibers occur in the form of bundles, except in the case of cotton, where cellulose in ultimate fibers is presented to us by nature. The fibers of different plants vary greatly in shape and size, from 0.5 to 200 millimeters in length and from 0.01 to 0.07 millimeters in diameter.

General Character. Cellulose fibers are physically very tough and chemically inert. These properties afford its marvelous suitability for the part it plays in nature and adapt it wonderfully for man's use in the arts. Sunlight, moisture, and air cause a gradual oxidation with the formation of oxy-cellulose, gases, and humus substances. Old papers and other cellulose materials deteriorate from these causes (1).

The various fibers have different chemical compositions, and there are therefore many varieties of cellulose, of which the simplest is an amorphous carbohydrate of the empirical composition $C_6H_{10}O_5$. This is combined with other non-nitrogenous groups in the various celluloses, which are generally classified as follows:

Classification. *Pecto-celluloses* (cotton, flax, hemp, ramie, etc.) yield pure cellulose upon hydrolysis, the pectic matter being dissolved.

This pectic matter consists of compounds of a carbohydrate nature about which not much is known. Pectin, found in ripe fruit, is precipitated by alcohol and gelatinized with boiling water; pectose, found in unripe fruit, is insoluble in water. They are both hydrolyzed by alkalies and acids to intermediate compounds and finally to hexoses and pentoses (2).

Ligno-celluloses (jute, straws, woods, etc.) contain the simple cellulose molecule chemically combined with lignin. This is a compound of the formula $ROCH_3$, in which R is probably aromatic. These celluloses are characterized by forming compounds with the halogens which are soluble in dilute sulphite or alkaline solutions, the pure cellulose thus being freed.

Cuto and adipo celluloses (cork, skins of fruit, etc.) are very complex and contain waxy products.

Cellulose is also found in peat, humus, etc., and possibly in certain animal tissues in the form of tunicin.

Cellulose Raw Materials. From natural products cellulose may be isolated by several methods of treatment. The best, and that generally adopted for quantitative analysis, is the Cross and Bevan method (3), which consists of, first: hydrolysis by boiling dilute alkali; second, chlorination; and third, boiling with dilute sulphite solution. The amounts of anhydrous cellulose and the other constituents in certain fibrous materials, together with the other data, are presented in the following table (4):

VEGETABLE FIBROUS MATERIALS[1]

		Dimensions of Fibers		Composition of Air-dried Substance								
Class	Name	Length mm.	Diam. μ	Ash	Moisture	Cellulose	Wax Oil	Resin	Water soluble	Protein	Pectic matter	Lignin.
Pecto Celluloses	Cotton	20– 40	10–24	0.1–1.7	6–8	84–91	0.3–0.6		0.1–5.8	0.5–1.5	0.3–0.8	
	Ramie	60–250	20–80	5.6	10.1	66	0.6		10.3		12.7	
	Flax	4– 66	12–26	0.7–1.6	8.–11	71–83	0.5–2.5		3.6–6.0		2.7–9.4	
	Hemp	5– 55	16–50	0 8	8.9	78	0.6		3.5		9.3	
	Manila	3– 12	16–32	1.0	11.9	65	0.6		1.0		21.8	
Ligno Celluloses	Jute	1– 5	20–25	0.7	9.6–12.6	61–64	0.4		1.0–3.9			21–25
	Wheat Straw			4–6	10–14	44–51	1.2–1.6		8.5	2–3		22–28
	Esparto	0.5–3.5	7–18	3.3–3.7	8–10	46–50	2.1–2.7		10–12			26–30
	Bamboo			5	9	53	0.8		11			26
	Woods			About						About		
	Beech			0.5	12.6	45–53	0.4		2.4	1		30–39
	Birch			0.5	12.5	55	1.1		2.7	1		28
	Elm			0.5	10.7	48–55	0.9		2.5	1		31–38
	Linden			0 5	10.1	53	3.9		3.6	1		29
	Oak			0.5	13.1	40–48	0.9		12.2	1		26–34
	Poplar			0.5	12.1	63	1.4		2.9	1		20
	Fir			0.5	13.9	50–57	About 1	0.8–1.6	1.3	1		18–25
	White Pine			0.5	12.9	53–58	About 1	3–6	4.1	1		17–25
	Spruce			0.5	10–13	53–60	About 1	1.9–2.2		0.7		30

[1] Where decimal figures are given in the above table, it is to be understood that these represent only a summary of analyses by different observers, and not the limits of contents. Where two figures are given, these represent the approximate limits of the amounts of this constituent, in a number of analyses.

The figures given under lignin for jute and wheat straw also include the pectic matter.

The figures given under lignin for esparto and bamboo also include protein and pectic matter.

The figures given under lignin for different woods also include pectic matter.

It will be noted that the figures given for the percentage of cellulose for spruce and poplar are higher than for other woods, which indicates the reason why these woods are so much used for paper making; while the percentages of lignin in beech and other hard woods are higher than found in evergreens.

These and other fibers are used in paper-making and in the textile industries, the cellulose being separated and purified by different treatments, such as the purification of cotton, the retting of flax, the sulphite and soda processes for wood, etc., but the discussion of these does not properly belong to this chapter. It may be remarked however that pure unaltered cellulose is not obtained by most of these treatments, the products from wood, for example, containing such impurities as oxycelluloses, resin, pentosan, and other substances.

In the cellulose industries as considered in this article, the principal raw materials are cotton waste, cotton yarn, linters, cotton hull fiber, tissue paper, and chemical wood pulp.

Normal Cellulose. The purest form of cellulose is generally stated to be Swedish filter paper, but on account of the severe treatment this undergoes in the process of purification the cellulose itself is attacked and slightly altered. Cotton fiber purified of its pectic bodies, fat, and nitrogenous matter by the mildest possible treatment, furnishes the purest cellulose, and Cross and Bevan have recently suggested for "normal cellulose" cotton as prepared for calico manufacture (5).

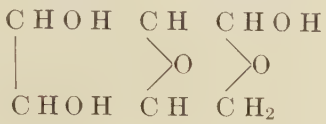
Composition. This purified cellulose contains 0.1–0.5 per cent inorganic matter which remains as ash upon burning. Cellulose is found by ultimate analysis to have the composition:

Carbon	44.2 per cent
Hydrogen	6.3 "
Oxygen	49.5 "

Constitution. The molecular weight is unknown, and cellulose is regarded as a polymeride of a formula $(C_6H_{10}O_5)_n$ in which n is very large; or as a colloidal aggregate, the constituent groups of which react, the equilibrium of the aggregate being modified by the process of the reaction. The question is of great significance, as cellulose and starch are the most important colloids, and the whole subject of Colloid Chemistry, in spite of much investigation, is still largely an unknown territory. We do not even know whether our commonly accepted theories for crystalloid substances will apply to colloids, and wonder whether we must return in part, at least, to the "vital" chemistry of our forefathers. At all events, we cannot present an accurate picture of the cellulose molecule, so in all discussions of reactions it must be understood that any equations used are simply intended as an approximate representa-

tion of what takes place. We do know that of the five oxygen atoms, three react as hydroxyl groups, and two as CO groups.

Green's Formula (6):



is a useful generalization.

Properties. Cellulose is a white, amorphous, firm, elastic substance of specific gravity 1.6 (7). It burns quietly with a luminous flame and is a poor conductor of heat and electricity, dielectric constant 7. Migrates to anode (8). Specific heat 0.319. Heat of combustion to CO_2 and H_2O 4208. calories.

Viewed under polarized light, cellulose flashes up in different colors, thus being distinguished from its derivatives, such as nitrates which are gray under polarized light.

Cellulose fibers absorb liquids very readily, the air from the cell canals being displaced. This absorbtive power is increased by proper preparation of the fiber, and is an important point in several industries, problems of capillarity and osmosis being involved.

Cellulose is hygroscopic, the different kinds containing 6–12 per cent moisture under ordinary conditions. Removal of the moisture is effected by drying at 100° C., and dessication over conc. sulphuric acid. The hygroscopicity varies widely with the different kinds of fiber, the method of treatment they have received, and the atmospheric humidity. This subject of " water of condition " is of extreme importance in the textile industries, to which a full discussion of it more properly belongs. The " water of condition " of cotton at 20° C. and 50 per cent relative humidity is 6 to 7 per cent; it reaches 21 per cent in an atmosphere saturated with moisture (9).

Another important aspect of Cellulose Chemistry with respect to the textile industries is the fixation of coloring matters. The phenomena are not completely explained, whether mechanical absorption in the cell canals, adsorption compounds, or true chemical reactions. Mordanting is a partly physical and partly chemical phenomenon (10).

Cellulose is resistant to the action of moderate dry heat, but is attacked by heating in water under high pressures (11). By heating cellulose decomposition begins at 140° C., and at 200° this proceeds rapidly, giving off gases (12). Upon distillation the greater part of the volatile products are driven over between 250 and 300° C., and carbonization is completed at about 380° C. The products are approximately as follows (13):

	Per Cent	Per Cent
Charcoal	38.82	20–40
CO_2	10.35	10
C_2H_4	0.17	0.2
CO	4.15	4
CH_4	0.27	0.3
Acetone	.07	0.2–0.3
Acetic Acid	1.39	3.1
Organic Substances in Acetate	5.14	8–5
Tar	4.18	7–4
Water	34.52	34
Loss	0.94	
	100	

It will be noted that no methyl alcohol is included in the products.

Cellulose is destroyed by fermentation, probably according to the following reactions:

$$C_6H_{10}O_5+H_2O\rightarrow C_6H_{12}O_6\rightarrow 3CH_4+3CO_2 \quad (14).$$

In this way marsh gas is formed in nature.

Solvents. Cellulose is insoluble in all ordinary solvents and no true solution can be made from which it may be precipitated in unchanged condition. It is dissolved by heating in a concentrated (40 per cent) solution of zinc chloride (15); in a cold $33\frac{1}{3}$ per cent zinc chloride solution in hydrochloric acid (16); in a solution of copper hydroxide in ammonium hydrate (2 per cent CuO, 10–15 per cent NH_3) (17); and in certain other ammoniacal solutions of metallic salts. These solutions are in the nature of double salt formations.

Reactions. Cold, dilute acids have an almost inappreciable action, a slight formation of adsorption compounds taking place.

Mineral acids of 10 to 40 per cent acidity form hydrocellulose.

$$(C_6H_{10}O_5)_{n+x}H_2O\rightarrow(C_6H_{10}O_5)_n(H_2O)_x$$

a friable, white powder which is more reactive than cellulose, the aggregate having been modified by hydrolytic action (18).

Stronger acids, 60 to 80 per cent, tend to form hydrates of cellulose (19).

Concentrated acids form esters or cellulose acids.

$$(C_6H_{10}O_5)_{n+x}H_2SO_4=C_{6n}H_{10n}O_{5n-x}(SO_4)_{x+x}H_2O.$$

Cellulose sulphuric acids are very unstable and cannot be isolated from solution in the acid. Prolonged action, followed by dilution with water and boiling, converts the cellulose into glucose (20).

Concentrated nitric acid produces cellulose nitrates, the limit of reaction being:

$$C_6H_{10}O_5+3HNO_3=C_6H_7O_2(NO_3)_3+3H_2O.$$

This reaction, of great technical importance, is always carried on in practice with a mixture of sulphuric and nitric acids. The sulphuric acid

takes up the water produced in the reaction, and also tends to form cellulose sulphuric acids, which react with the nitric acid in the mixture, forming cellulose nitrates and regenerating the sulphuric acid (21).

The important factors are:

(*a*) Strength of the acid.
(*b*) Temperature of the acid.
(*c*) Time of nitration.
(*d*) Proportion of acid to cellulose.

By varying these conditions products of widely different properties are obtained.

(*a*) The proportion of sulphuric to nitric acid is of minor importance, the essential thing being that there is an excess of the latter. Proportions of 1 : 1 to 3 : 1 are used. The effect of the acid mixture depends mainly upon the total acidity, or conversely upon the percentage of water, which varies from 10 to 20 per cent. A low percentage of water causes a nitration approaching more closely to the limit of reaction. A higher water content gives a lower percentage of nitrogen in the product.

(*b*) Increasing the temperature increases the rate of reaction. Thus a nitration in cold acid may require twenty-four hours to be complete, while with the same acid mixture at a temperature of perhaps 40 degrees, the reaction would be complete inside of an hour. As the temperature of the acid bath increases, secondary reactions occur, so that the properties of the product are modified.

(*c*) As indicated above, the time of nitration depends very largely upon the temperature. In practice cellulose is usually nitrated for about thirty minutes, but in certain cold processes for as long as twenty-four hours.

(*d*) Thirty to 50 parts of acid to one of cellulose are used, and this proportion is sometimes increased. It is important to use an excess of acid.

The cellulose used is purified cotton waste, linters, hull fiber, cotton yarn, or tissue paper.

Three different forms of apparatus are used:

1. Iron or earthenware pots, into which the acid is run and the cellulose then immersed. At the completion of the nitration the material is dumped into centrifugal machines, and the excess of acid removed.

2. Centrifugal machines, the machines being started in motion after nitration is complete.

3. In the Thomson process stoneware pans, the acid being removed by displacement with water.

After nitrating by any of these processes the product is thoroughly washed in water and usually boiled to remove unstable by-products.

When first made, cellulose nitrates were very unstable and dangerous. This was overcome by proper purification, consisting of pulping, as intro-

duced by Abel, and by long-continued boiling, preferably in slightly acid water. Bleaching with hypochlorite is sometimes necessary.

The washed product is dried by pressure and absorption of the water by bibulous materials, by a current of air, or by displacement of the water by grain alcohol. The yield varies with the percentage of nitrogen. Theoretical yields vary from 160 to 210 parts. In practice these yields are reduced by solution in the acid, secondary reactions, and mechanical losses, and vary between 130 and 175 parts.

Treatment of cellulose nitrates with sodium sulphide or ammonium sulphide solutions removes the nitrate group and regenerates cellulose hydrate (22).

The halogen acids form hydrocellulose, as would be expected from the above. A specific reaction is caused by a solution of hydrogen bromide in carbon tetrachloride which acts very energetically, forming brommethyl-furfurol (23).

Acetic anhydride, with a condensing agent, dissolves cellulose with formation of cellulose acetates (24).

$$C_6H_{10}O_5+3(CH_3CO)_2O=C_6H_7O_2(O_2C.CH_3)_3+3CH_3.COOH.$$

Cellulose formates and benzoates are similarly prepared (25).

Mixed esters, such as aceto-sulphates, aceto-nitrates, etc., have also been made and investigated.

Dilute alkalies form small quantities of indefinite adsorption compounds, about 1 per cent alkali being absorbed.

Solutions of caustic alkalies (10–25 per cent NaOH) cause a structural change in the fibers, a phenomenon first described by Mercer and of considerable importance in the textile industries, as the fiber held under tension assumes a lustrous appearance. The mechanism of mercerization has not been completely explained. It appears that a sodium additive compound of cellulose, probably ($C_6H_{10}O_5.2NaOH$) is formed and is hydrolyzed by water to cellulose hydrate (26).

Stronger alkaline solutions, 30 per cent or more NaOH, dissolve cellulose with formation of so-called acid cellulose (27).

Fused (concentrated) caustic alkalies give acetic and oxalic acids.

A most interesting reaction and one of increasing technical importance is the formation of cellulose thiocarbonate. Cellulose treated with sodium hydrate reacts with carbon bisulphide, the product dissolving in water.

$$C_6H_{10}O_5+NaOH+CS_2=CS(SNa)-O.C_6H_9O_4+H_2O$$

This thiocarbonate or alkali-cellulose-xanthate gives very viscous solutions which decompose on standing, by heating, or upon treatment with acid, into cellulose hydrate, NaOH, and carbon bisulphide (28).

Cellulose is quite unaffected by reducing substances.

Cellulose is resistant to oxidation, but long-continued action of certain oxidizing agents produces deep modifications.

Ozone, bromine, chlorine and chlor acids cause oxidation. Nitric acid of 1.1 to 1.3 specific gravity at 80 to 100° forms oxycellulose. Chromic acid forms oxy-cellulose. Potassium permanganate forms oxy-cellulose, caramel, oxidized carbohydrates, oxalic acid, carbon dioxide, etc. Only 30 to 40 per cent of oxy-cellulose has been obtained, for with more drastic treatment to secure higher yields the remainder of the cellulose is oxidized to oxalic acid and carbon dioxide (29).

Derivatives. From the foregoing summary of cellulose reactions it will be seen that numerous derivatives are obtained which are briefly described in the following:

Cellulose hydrates, which are formed by mechanical reduction of fibers in water, action of salt solutions, mercerization, precipitation from solutions, regeneration from esters, or action of acids, are more reactive than cellulose. They take up more direct colors and are more reactive with substantive colors such as benzopurpurin, give characteristic coloration with iodine, have higher copper numbers, and yield furfural on distillation with hydrochloric acid (30).

Hydrocellulose is less hydroscopic than cellulose, very slightly affected by alkalies, gives a blue violet color with $ZnCl_2$: I, which washes out with water, does not fix basic colors, and gives characteristic reduction coefficients (31).

Oxy-cellulose $C_{18}H_{26}O_{16}$ is a white flocculent substance which forms gelatinous hydrates with water and dissolves in dilute alkali. There are several modifications, and the cellulose complex has been altered. Found in nature in flowers, woods, straws, etc. (32).

Other derivatives of minor importance, are hydral cellulose, acid cellulose, and cellulose peroxide.

A nitric ester was first made by Braconnot (33) in 1833; again by Pelouze (34) in 1838, and developed by Schönbein (35) in 1846, who was the first to use a mixture of sulphuric and nitric acid, and is generally credited with the discovery of cellulose nitrate. The literature of these derivatives is very extensive. There has recently appeared an excellent work on their technical use, "The Nitrocellulose Industry," by E. C. Worden. Distinguished researches on the subject have been those of Vieille (36), Eder (37), Lunge (38), de Mosenthal (39), Will (40), Hake and Bell (41), Haeussermann (42), Berl and Klaye (43), and Mendeléeff (44).

The following gives a summary of the composition, solubilities, and other characteristics of important commercial pyroxylins.

As ordinarily prepared, cellulose nitrates have the unaltered appearance of the original fiber, but are harsher to the touch. The specific gravity is only slightly higher than that of cellulose, the volume rather

than the density being increased in nitrating. They ordinarily float in water, on account of the presence of air in the fibers. They are less hygroscopic than cellulose; thus a pyroxylin with 13 per cent of nitrogen has about 1.5 per cent water of condition, and a pyroxylin with 11 per cent of nitrogen, about 3.5 per cent.

These derivatives burn very rapidly, the rate of combustion increasing with the percentage of nitrogen. It is to be noted that nitration is a progressive phenomenon, and that we cannot recognize any definite steps in the reactions, so that any names such as tri-nitrate, hexa-nitrate, penta-nitrate, etc., are not well founded.

The maximum theoretical percentage of nitrogen is 14.14 per cent, but this has never been reached in practice. The most highly nitrated products contain 13.3 to 13.7 per cent of nitrogen, and are known as guncottons. Soluble in acetone and ethylacetate, but insoluble in ether-alcohol, nitroglycerine, and other solvents of the lower nitrates. Guncotton is ignited by shock, differing in this respect also from other cellulose nitrates.

Pyroxylins, as used for smokeless powders and gelatine dynamites, contain 12.4 to 12.8 per cent nitrogen, and are less soluble in wood-alcohol, amylacetate, and camphor-alcohol than lower nitrates. Pyrocellulose is the standard pyroxylin of this class, containing 12.6 per cent of nitrogen.

Soluble pyroxylins, called variously collodion cotton, soluble cotton, and varnish cotton, contain close to 12 per cent of nitrogen, and dissolve in ether-alcohol, amylacetate, wood-alcohol, and other solvents to solutions of less viscosity than any other pyroxylins.

Celluloid pyroxylins contain 10.8 to 11.6 per cent of nitrogen, and are soluble in all these solvents, but give solutions of greater viscosity than the varnish cottons. It may be noted here that two pyroxylins with the same percentage of nitrogen may show very different solubilities and viscosities, due to secondary reactions in the nitration.

Pyroxylins containing 10 per cent of nitrogen and soluble in grain alcohol alone may also be made, but have not found any applications. Cellulose nitrates containing less than 10 per cent of nitrogen are not soluble in organic solvents. A hydrated nitrate of cellulose with about 3 per cent of nitrogen has been patented by Herstein (45) and this product is soluble in solutions of alkalies and certain phenols.

A cellulose acetate was first made by Schützenberger in 1869 (46), and again by Franchimont in 1881 (47), and investigated by Cross and Bevan. A catalytic agent is necessary to cause cellulose to react with acetic anhydride, the usual procedure being to treat the cotton with acetic anhydride and a small percentage of sulphuric acid, the cellulose dissolving in the mixture and the acetate being precipitated by dilution with water. Cellulose acetate thus prepared is a tough, white, pithy substance, quite resistant to alkali, but saponified by alcoholic potash.

It is not attacked by dilute acids, but is hydrolyzed by 50 per cent sulphuric acid and hot concentrated hydrochloric acid. Yellow-brown colorations are given with zinc chloride-iodine reagent. Soluble in chloroform, glacial acetic acid, epichlorhydrin, nitrobenzol and acetylene tetrachloride. Cellulose acetates, soluble in acetone and in alcohol, are also made (48). Identified by saponifying, acidifying, and distilling off the acetic acid, this method being employed for analysis (49). The formates, benzoates, and other organic esters resemble the acetates in physical character, but differ in solubilities.

Viscose is the name given to the thiocarbonate product, the formation of which has been described above. When regenerated, it is a hydrate of cellulose.

Formaldehyde cellulose, sulpho-hydro cellulose, and tetraphenyl cellulose have also been prepared, but do not possess any commercial value.

Analytical. Cellulose is identified by developing a blue color with a solution of iodine in potassium iodide in admixture with zinc chloride (50).

The quantitative estimation of cellulose has been described above, and also the identification of hydrate, hydro, and oxy-cellulose, and other derivatives. The various kinds of fiber are distinguished by microscopic examination (51).

Important determinations are: 1st, Percentage of moisture, determined by drying the cellulose at 90–100 ° C. and dessication over sulphuric acid (52). 2nd, Percentage of ash obtained by incineration (53). 3rd, Estimation of fat, wax, and resin by extraction in a Soxhlet apparatus (54). 4th, The " copper number " by reduction of Fehling's solution (55). 5th, "Acid number " or the consumption of sodium hydrate upon boiling (56). 6th, The yield of furfural upon distillation with hydrochloric acid (57). 7th, Fixation of basic coloring matters such as methylene blue (58).

Cellulose industries are classified in the following table according to their relationship to the characteristics of the parent substance.

It may be noted again that cellulose is a structural material, and it is upon considerations of form and physical characteristics that these industries mainly depend.

CLASSIFICATION OF INDUSTRIES

Physical Characteristics of the Fiber

Textiles — Mercerized Fabrics, *Vegetable Parchment* — Paper

Change in Form after Solution

Vulcanized Fiber	Artificial Leather
Lamp Filaments	Photographic Films
Artificial Silk	Pyroxylin Plastics
Cellophane	Acetate Plastics
Pyroxylin Solutions	

Change in Chemical Behavior

Explosives

Decomposition of Cellulose Complex

Distillation of Wood. Oxalic Acid. Alcohol.

INDUSTRIES DEPENDING ON THE PHYSICAL CHARACTERISTICS OF THE FIBERS

Textiles. These comprise one of the most important of all industries, but as they are described elsewhere in this volume, in Chapter XLII, no description of them will be given here. The industries are mostly based on mechanical principles, but the chemistry is important in such matters as the water of condition, bleaching, dyeing, etc.

Mercerized Fabrics. This branch of the textile industries has become of increasing importance in the last few years. In practice, cotton is mercerized generally in the form of fabric, and also as yard. In the former, the cotton cloth is passed through a cold bath of 30 per cent sodium hydrate and afterwards washed with hot and cold water. The cloth is kept under tension by being drawn along through a series of rolls and supported on a frame with side clamps (59).

Paper. Another very important class of industries is the preparation of the many classes of paper, but this also falls outside of our subject, as it is covered in Chapter XLIV. The chemistry of this industry is very diversified and of great importance.

Vegetable Parchment. This product is obtained by a short immersion of unsized paper in 75–84 per cent sulphuric acid, followed by immediate washing in water and drying. A layer of semi-transparent gelatinous amyloid or cellulose hydrate is thus deposited on the surface, and the paper becomes tough and resembles in appearance natural parchment. In the process the sulphuric acid is contained in lead-lined tanks, and the paper is unrolled and drawn through the bath and then between rolls of acid-resisting material into a bath of wash-water. The sheet is dried under tension. Thick sheets are made by pressing together layers of paper which have just been parchmentized.

The important factors are the condition of the paper, the strength of the acid, the temperature of the acid, the time of immersion, and the completeness of washing. Under- or over-treatment by the acid must be avoided and no trace of acid should remain in the parchment.

It is used for packing greasy materials, for semipermeable membranes, and in general as a substitute for natural parchment.

A similar product is also obtained by mechanical treatment: sulphite pulp is beaten in an engine into a slimy mass, and formed into sheets of parchment paper. When made in tissues this comes upon the market by the name of pergamyn. A similar product is cellulith. In preparing

this the pulp is beaten until the fibers entirely disappear. It is then heated, strained, and allowed to settle. The mass which settles is then thoroughly dried, forming a horny mass which is somewhat similar to vulcanized fiber.

Vulcanized Fiber. This is prepared by treating unsized, unloaded, rag paper in a warm solution of zinc chloride in water. The solution contains 65 to 70 per cent $ZnCl_2$ and is maintained at a temperature close to 40° C. A roll of paper is unwound, passed over heated cylinders and then through the bath, and is then rolled up on large heated cylinders until the desired thickness is obtained. The surface is gelatinized so that the paper welds together on the receiving drum where it is squeezed by the pressure of a heavy roll above it. The sheet is then cut off the drum and is washed in zinc chloride solutions of diminishing concentration, and finally in pure water until no test, or a very faint test for chlorides is obtained. This washing treatment is slow, depending on the size of the sheet; $\frac{1}{4}$ inch material takes three or four weeks, and 2 inches six to eight months. Zinc chloride is recovered from the stronger wash waters by using them progressively. This matter of washing is of the greatest importance on account of the danger of blistering, which is thought to be caused by osmotic pressure. If the washing is not complete, inferior fiber is the result.

The product shrinks on drying to about half its original size and is remarkably homogeneous. It comes on the market in reddish brown, gray, or black colors, which are obtained by using differently colored papers containing iron oxide, lamp black, or other coloring matter. The product is very hard, of a horny consistency and is worked by sawing, turning, etc., may be threaded and embossed, but is not properly plastic to heat.

The specific gravity varies from 1.3 to 1.5; the tensile strength from 8000 to 13,000 pounds per square inch, and the crushing strength from 35,000 to 45,000 pounds per square inch. Fiber has a dielectric strength of 200 to 400 volts per mil. It is oilproof but not waterproof, absorbing 20 to 50 per cent of its weight of water upon prolonged immersion, but dries again to its original size; it is not soluble in any organic solvents and is very resistant to chemical action except the hydrolytic action of mineral acids on long exposure.

Fiber finds a wide variety of uses, such as for trunks, bags, handles of cheap cutlery, receptacles, such as waste baskets, and for a considerable number of engineering purposes, notably gears, washers, valves, etc. The annual production in the United States is over 15,000,000 pounds.

Lamp Filaments. When the possibility of incandescent electric lighting was first realized a thorough search was made for the most suitable material for making filaments. Lane-Fox and Swan, in England, produced a carbon filament by acting upon cotton with zinc chloride, and

this practice became the usual method of producing filaments for incandescent lights.

A viscous solution of cellulose is prepared and forced through capillary orifices into a precipitating bath. The fibers thus produced are washed thoroughly to remove all traces of zinc chloride, dried, spun into filaments, and carbonized by heating between layers of sawdust to exclude air. Filaments of a brown translucent appearance resembling human hair are thus produced.

These filaments are now being displaced to a large extent by ductile tungsten, but the manufacture is still of very large proportions. The process is carried on by the electric companies who manufacture the lamps, and an idea of the extent of the industry may be gained from the fact that one factory of the General Electric Company produced 100,000 lamps per day.

Artificial Silk. This class of materials is composed of cellulose filaments, produced by several processes, and resembling the luster and qualities of natural silk. Silk differs from other natural fibers in being a continous solid thread, and many unsuccessful experiments to imitate it had been made. In 1884, Chardonnet (61) produced the first successful fiber, and founded the artificial silk industry, which has grown rapidly and has become to-day very important.

There are three successful processes in use, all of them following the procedure of preparing a solution of cellulose, forcing it through a minute orifice, and precipitating the stream of solution, thus forming a fiber. The processes differ by the method of obtaining the cellulose solution (*a*) cellulose nitrate, (*b*) cuprammonium and (*c*) thiocarbonate.

Cellulose Nitrate Silks. These were the first artificial silks to be made, and still constitute a very important branch of the industry. The two principal modifications of this process are those of Chardonnet and Lehner. In both, cotton waste or linters is nitrated in a mixture of sulphuric and nitric acid, usually in centrifugal machines by which the excess of acid is removed from the pyroxylin produced. Details of the acid bath, temperature, and time of nitration are given in the patents. The product is washed thoroughly in water and dried with warm air or grain alcohol. The pyroxylin thus prepared is dissolved in a mixture of ether and alcohol in suitable mixers, a 20 per cent pyroxylin solution being produced, and carefully filtered to remove all dirt, or other solid material. The clear solution is forced by hydraulic pressure through orifices about 0.09 mm. in diameter and coagulated with warm water or moist air. The fibers are washed in water, denitrated in a bath of alkaline sulphide solution, thoroughly washed in tepid water, dried, and spun into thread, the whole process being carried out by special machines of intricate design. Bleaching is necessary to obtain the proper color. The filaments thus produced are white and lustrous, but not as strong as natural silk. They contain 0.05–0.2 per cent of nitrogen and 10–12 per cent water of con-

dition. The breaking strain is greatly diminished by wetting with water.

Cuprammonium Silks. This process was first patented by Pelouze, and has been developed by Fremery, Urban, Bronnert, Linkmeyer, and others, the product being called " Lustra Cellulose " or " Glanzstoff."

The cuprammonium reagent is usually prepared by exposing thin sheet copper in cylindrical towers to the combined action of ammonia and air. The tower is jacketed and cold brine circulated. Concentrated ammonium hydrate trickles down over the copper, and cool compressed-air is passed up through the mass. Purified cotton is dissolved in this reagent, and the solution, which contains about 8–10 per cent of cellulose, 2–3 per cent of copper and 10–15 per cent NH_3, is purified by filtration. A prior mercerization of the cotton promotes solution in the cuprammonium. It is forced through capillary orifices with a pressure of about 50 pounds per square inch, and precipitated in a bath of acid or alkali. The fibers are now thoroughly washed in dilute acid and water, and dried under tension at moderate temperatures.

The tensile strength seems to be higher than that of the pyroxylin silks, and the water of condition lower, about 9 per cent. It gives no reaction in the diphenylamine test, while pyroxylin silks are colored deep blue.

This process has overtaken the pyroxylin silks in output, but has now been passed by viscose silks.

Viscose Silks. This process has been developed since the year 1907, and depends on the cellulose thiocarbonate solution discovered by Cross, Bevan and Beadle, in England, in 1892.

The raw material is chemical wood pulp which must be as pure cellulose as possible. The pulp is put into wire baskets, or between perforated plates, and immersed in sodium hydrate solution in iron tanks for several hours. The excess of lye is removed by pressure or whizzing until the mass weighs about three times the original pulp. It is then broken up in a kneading-machine and allowed to stand to complete the reaction. The pulp is now put into a mixing-machine, and about 30 per cent carbon bisulphide added. After being thoroughly mixed, soft water is added with or without the addition of sodium hydrate, in amounts which will give the desired percentage of cellulose and of sodium hydrate. The yellow solution is now stored in tanks and aged.

The solution thus made is formed into fibers in the same manner as that described above, the precipitating bath consisting of acid, or, in recent developments, alkalies. The fibers are then thoroughly washed, spun into threads, bleached, dyed, etc.

Viscose silk as first made was very weak, but now has a greater tensile strength than either the cellulose nitrate or cuprammonium silk. The water of condition is 10–12 per cent. This process seems to yield a cheaper product than the foregoing, and the difficulties which have hindered its development have been largely overcome, so that to-day the viscose pro-

cess is supplanting the older ones and seems to have a brighter future.

Artificial silks are produced in all colors and designs and are continually finding new uses, but are not suitable for all purposes instead of the natural silk. There are about thirty factories in the world, principally in England, France, Belgium, and Germany, there being one large factory in the United States. The total output of artificial silks is at the present time, 1914, about 14,000,000 pounds per year (62).

Cellophane. Transparent sheets are produced according to a French process by flowing a solution of viscose on a suitable surface and precipitating the cellulose hydrate. The process is similar to the manufacture of viscose silk except as to the form of the finishing product. Cellophane, either colorless or delicately colored, and with polished or embossed surface, is used principally in wrapping confectionery.

Pyroxylin Solutions. As indicated in the description of the cellulose nitrates, they are soluble in various liquids, of which the chief commercial solvents are wood-alcohol, acetone, amylacetate, ethylacetate, ether-alcohol, and solutions of camphor in grain alcohol. Solutions of various grades of pyroxylins of maximum solubility, "varnish cotton," in these solvents come upon the market for various purposes, such as (*a*) collodion, (*b*) lacquers, (*c*) bronzing liquids, (*d*) enamels, (*e*) dopes and cements. The solutions are prepared by dissolving the pyroxylin in the solvent in mixing-machines or tumbling-barrels, and are purified by settling or filtration.

Dopes. Dopes, or heavy pyroxylin solutions are used principally for finishing leather and coating airplane fabrics, pyroxylin cement for leather is used in belting, etc. These consist of 6 to 10 per cent pyroxylin in solvent mixtures which may contain wood alcohol, amyl acetate, acetone, and benzine.

Pharmacopœial Collodion. This article, which comes upon the market in several varieties and under different names for treatment of cuts, etc., is a 3–5 per cent solution of pyroxylin in a mixture of ether and alcohol, the ordinary proportions being three parts of ether to one of grain alcohol. The pyroxylin is very soluble, made by nitrating purified cotton.

Various formulas are given in the pharmacopœias of the different countries for making elastic collodion. One to 3 per cent of castor oil is added to the solution, and also in some formulas Canada Balsam or turpentine. Other ingredients are sometimes added to impart the desired properties.

Lacquers. These are solutions of pyroxylin and resins, and are used for coating metals, wood, etc. They are classified according to their method of application, as dip, spray, or brush lacquers. The essential difference between these classes is that the first-named are very much thinner, so that the article to be coated may be dipped in the lacquer and the excess drained off without leaving any drip; while the solvent of the brush lacquers must be less volatile, so that the coat may flow out before drying.

The industry depends upon the proper use of solvents, and of these amylacetate is the most important, because it is slow-drying and not hydroscopic. The use of this solvent was patented in 1882 by J. H. Stevens, and the business was first developed by Richard Hale and the F. Crane Chemical Company. Besides amylacetate the solvents used are wood-alcohol, acetone, fusel oil, and diluents such as benzine. A mixture of solvents is used which will yield a clear film on drying.

The pyroxylin used is of maximum solubility and of low viscosity, containing about 12 per cent of nitrogen. It is prepared by nitrating purified cotton waste, yarn, or other pure form of cellulose. Celluloid scrap is also used. The other solid ingredient is a resin, such as shellac, copal, etc.

Such a lacquer deposits an exceedingly thin film of great tenacity and durability. These lacquers are used for coating brass goods, silverware, wood-surfaces, and for similar purposes.

Bronzing Liquids. These are thin solutions of about 3 per cent of pyroxylin in suitable solvents, usually containing a small percentage of resin. Bronze powder, usually aluminum, is thoroughly mixed with a bronzing liquid, and applied with a brush. It finds a wide use for gilding radiators and other metal articles. Various colors are made to imitate the different metallic finishes.

Enamels. By adding pigments and other coloring matters to the lacquers described above, pyroxylin enamels are produced in every color and in many grades. Beautiful, hard, durable finishes are thus obtained on wood and metals, and the use of these solutions is steadily increasing (63).

Artificial Leather. This material, which is made in many grades imitating all kinds of natural leather, consists of a fabric with a tough, flexible coating in which pyroxylin is usually the essential ingredient. A dope, or thick solution of pyroxylin in proper solvents, is applied by means of a spreading device to the surface of the fabric as it unwinds from a roll. The solvents evaporate and the surface is embossed or otherwise ornamented by being passed through calendar rolls or embossing presses. The dope usually contains castor oil or similar substance.

This industry has become a very important one both in foreign countries and in the United States, and very handsome products are obtained. About 50,000 yards of pyroxylin artificial leather are made per day in this country. Pyroxylin solution is also applied to real leather in producing enamel and patent leather. The dope contains of a mixture of pyroxylin, castor or other oil in wood-alcohol, amylacetate, fusel oil, or benzine and pigments to obtain the desired color effects. The solution containing 6–10 per cent of pyroxylin (64).

Photographic Films. In the development of photography a flexible support for the emulsion had long been desired, and was first produced by H. Goodwin in 1887, U. S. Patent 610861. The manufacture of flexible supports of photographic films was introduced by the Eastman

Kodak Company, and has reached a marvelous development, so that to-day pyroxylin photographic and moving-picture films form an enormous industry.

The pyroxylin is made by nitrating purified cotton waste or other cotton cellulose, and must be of great solubility, the criteria being similar to those obtaining for varnish cottons. A solution is made of pyroxylin and camphor in a mixture of wood-alcohol, amylacetate, and other solvents, and this is poured on a smooth surface and allowed to evaporate, forming a film. The surface used is either flat glass tables or a revolving drum with specially prepared surface. When dry the film is stripped off, slit into the desired width, and cut into lengths.

The manufacture of the film is attended with great difficulties, as the product must be entirely transparent, free from specks, and of uniform thickness, about 5/1000 of an inch. For moving pictures strips $1\frac{3}{8}$ inches wide and 1000 feet long constitute one reel. These are slotted to secure the intermittent motion through the photographing or projecting instruments, both positive and negative films being used. For ordinary camera work, films of various sizes are prepared. It is estimated that the daily production of photographic film in the world amounts to 150,000 to 200,000 square feet (65).

Cellulose Nitrate Plastics. Plastic materials with pyroxylin as a base were first made in England, by A. Parkes in 1855 and D. Spill in 1868. The methods were crude, and the full significance of the solvent power of camphor was not realized. The industry was really founded in this country in 1869, by J. W. and I. S. Hyatt, who investigated the action of camphor upon cellulose nitrates, and devised splendid mechanical methods for making these plastics, to which they gave the name celluloid.

Pyroxylin plastics, variously called celluloid, xylonite, pyralin, fiberloid, viscoloid, and other names, consist of a mixture or solid solution of cellulose nitrate and camphor, there being formed a loose union of the cellulose with the ketone group of the camphor, as first pointed out by R. C. Schüpphaus. The composition is 25–40 parts of camphor to 100 parts of pyroxylin, solution being obtained by the use of a liquid solvent, such as alcohol.

Cellulose tissue paper or purified cotton is nitrated in such a manner that the product contains 10.8–11.6 per cent of nitrogen, and hence of lower inflammability than any other commercial nitrate, is readily soluble in camphor-alcohol, and gives more viscous solution than varnish cotton. After thoroughly washing, to insure stability, the pyroxylin is dried and mixed with camphor and alcohol in suitable mixing-machines or between steel rolls, and various coloring matters, to produce the desired effects, are incorporated. The pasty mass is pressed into a block by hydraulic pressure under heat. It is then cooled, whereupon the material becomes very stiff, and is planed into sheets of any thickness from 5/1000

up to 1 inch or more. Mottled effects, to imitate tortoise-shell, etc., are produced by a mixture of two or more colors, and stratified materials imitating ivory, horn, etc., by placing together alternate layers of different colored materials. Almost every natural material may be imitated.

Celluloid is made in all colors, the principal classes being transparent, cream, ebony, ivory, pearl, amber, and shell. It is used for brushes, combs, and other toilet articles, hair ornaments, collars, automobile windows, and for other purposes too numerous to mention. There are about fifteen factories in the world making this class of materials, situated in the United States, England, France, Germany, Austria, and Japan. The total production throughout the world is 200,000–250,000 pounds per day.

Pyroxylin plastic is one of the strongest artificial materials, possessing a tensile strength of 10–12,000 pounds per square inch. It takes a beautiful finish and has great plasticity, softening upon heating, and regaining its strength and appearance upon cooling. It is molded in dies to any desired form, cut, sawed, turned in a lathe, etc. As now prepared it is very stable against the action of heat, but is readily ignited by a flame. It is very inflammable, but not explosive, except that when burned in large masses in an enclosed space inflammable vapors are given off which may burst into flame (66).

Acetate Industries. While pyroxylin plastics are expensive, cellulose acetate is much more so on account of the necessary use of the expensive acetic anhydride and the great losses of this substance. This fact, and inferiorities to pyroxylin materials in strength and plasticity, have greatly hindered the industrial development of cellulose acetate, so that it is still an almost negli ible factor.

Purified cotton or other form of cellulose is converted into the acetate by treatment with acetic anhydride and sulphuric acid in pots, and the product thoroughly washed and dried. The cellulose acetate is dissolved in chlorinated solvents in mixing-machines, the manipulation being similar to that of celluloid. Various ingredients to secure plasticity are added, but no one substance which imparts the remarkable properties that camphor does to cellulose nitrate has been found.

Cellulose acetate plastics thus prepared in sheets of varying thicknesses are practically non-inflammable, melting upon the application of flame, and burning very slowly, and ceasing to burn when the source of heating is removed.

Cellon is the name given to a cellulose acetate plastic in Germany, which is made to some extent in imitation of pyroxylin plastics. The most successful application has been for mo ing-picture films, to which purpose it is adapted on account of its non-inflammable character. Owing, however, to the weakness of the film as compared with pyroxylin film and other inferior qualities, together with its high cost, its use has been abandoned in the United States and is limited in other countries. Cellulose acetate

also finds considerable application in insulating fine wire and also for fabrics used in balloons and aeroplanes (67).

INDUSTRIES DEPENDING ON CHANGE IN CHEMICAL BEHAVIOR.

Explosives. The modern explosive industries are founded on the use of highly nitrated cellulose such as gun-cotton, gelatin-cotton, and other nitrates. As this industry is described in Chapter XL, it will not be considered in this article.

Industries depending upon decomposition of cellulose.

Distillation Products. In the discussion of reactions in Section I, the products of distillation of pure cellulose are given. It may now be noted that in distilling wood somewhat different products are obtained, on account of the presence of lignin, as shown in the following table:

DISTILLATION OF WOODS

	Evergreen. Per Cent	Hardwood. Per Cent
Charcoal	38	31–35
CO_2	10.1–10.3	10–10.9
C_2H_4	0.2	0.2
CO	3.8	3.3–4.2
CH_4	0.6	0.5
Methyl Alcohol	0.9	1.6–2.1
Acetone	0.2	0.2
Acetic Acid	3.2–3.5	6–7
Organic Substances in Acetate	8	6–8
Tar	8–12	8
Water	22–26	26–28

Hardwoods, on account of their higher content of lignin, produce more methyl alcohol and acetic acid than do evergreens and are consequently exclusively used for this purpose. Large steel retorts are used, either vertical or horizontal, or large ovens into which the wood is run on cars charged with hardwood cut into proper lengths. When distillation commences, water comes over first, then acetic acid, wood-alcohol, acetone, tar oils, gas, and heavy tar oils. The heating is continued up to about 350° C., the residue consisting of wood-charcoal. The distillate is separated into fractions by distillation and the fractions purified. Ten gallons of wood-alcohol, 200 pounds of acetate of lime, and 50 bushels of charcoal are obtained per cord of wood.

The wood-products industry is of great importance, being practically the entire source of these materials, and is very largely an American industry. See Chapter XXIII (68).

Oxalic Acid. This is made by heating sawdust or wood-chips with twice its weight of a mixture of caustic soda and caustic potash at

240 to 250° C., for one and one-half hours. The melt is dissolved in water and the sodium oxalate may be removed by crystallization; or calcium oxalate is precipitated by lime, filtered off, and the oxalic acid set free by sulphuric acid, and purified by recrystallization. One part of cellulose yields 1.2 parts of oxalic acid (69).

Ethyl Alcohol from Wood Waste. As noted above, cellulose may be quantitatively converted into glucose by treatment with sulphuric acid, so it would appear to be a simple matter to ferment the glucose and obtain ethyl alcohol. In practice the process is attended with great difficulties, so that little progress has been made until recent years. In the processes developed by Classen and by Tomlinson and Ewen these difficulties have been surmounted to a certain extent and the industry put upon a commercial basis, where it is now beginning to compete with alcohol from corn and molasses. Sawdust is treated with about 1 per cent of its weight of gaseous sulphurous acid in rotating cylinders. Steam is introduced, bringing the pressure up to about 100 pounds, and the mass is cooked until the maximum hydrolysis is effected. The gases are released and the material extracted with water, hydrolyzed, fermented and distilled. It is stated that one ton of sawdust produces 20 gallons of alcohol. The process has been developed in this country, and there are to-day two plants in operation, one in South Carolina and the other in Louisiana, the total product being 5000 gallons of alcohol per day (70).

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CHAPTER XLVI

EXPLOSIVES

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An explosive is a substance or mixture of substances which by proper means can be made to decompose with great violence in such a way as to produce useful results, such as shattering rock and other obstacles, or the propulsion of projectiles. A large number of substances which may be classed as explosives are now known to chemistry, but for practical purposes only those explosives which can be manufactured cheaply on a large scale, and which possess certain desirable properties, are of commercial importance.

With few exceptions all commercial explosives are in one way or another derivatives of nitric acid, being either simple definite compounds containing the radicals NO_2 or NO_3, or mixtures of an organic or inorganic nitrate with other substances which are easily oxidized. The most important commercial explosives may be grouped in the following classes:

1. Black powder and similar mixtures.
2. Explosives consisting of nitrocellulose or nitrostarch.
3. Explosives consisting in whole or in part of nitroglycerine, dinitroglycerine, diglycerine nitrate and other nitrated derivatives of glycerine (usually designated as dynamites).
4. Various aromatic nitro compounds, such as picric acid and trinitrotoluol.
5. Fulminants, primers, or detonators, of which mercury fulminate may be regarded as the type.

Explosives are put to widely different uses and no one explosive has been found which will answer all purposes, Dynamite cannot be used as a propelling agent in firearms, and smokeless powder is not used as a substitute for dynamite in ordinary blasting operations. Explosives suitable for military purposes must conform to requirements quite different from those demanded for technical purposes, and an explosive suitable for use in a stone quarry may be totally unsuitable for use in a coal mine. In consequence of these varying requirements and the differing character of the raw materials and end products, the explosives industry is divided between factories which are quite unlike in design, equipment, and methods of operation.

The effect of an explosion is produced by the sudden liberation of large quantities of gas which is at a high temperature acquired from the heat of the reaction. When confined in a small space this hot gas necessarily exerts an enormous pressure on surrounding objects.

Black Powder. Black powder, or ordinary gunpowder, was the only explosive in general use up to the latter half of the nineteenth century. It is said to have been discovered in the thirteenth century, but its origin as well as the identity of its inventor is involved in an obscurity which probably can never be cleared. The first powder mill is said to have been erected at Augsburg in 1340, and from that time to this black powder has retained, with very slight variations, the composition given to it by the first powder makers. Although inferior in strength to many explosives recently discovered it is still being manufactured on an enormous scale.

For a long time after its discovery black powder was used exclusively for military purposes. Its peaceful application to the mining industry began about two hundred years ago.

Composition. Typical black powder is an intimate mixture of potassium nitrate, wood charcoal, and sulphur. It is generally manufactured in granular form, the individual granules having a slight coating of graphite. The composition of black powder varies slightly in different countries. Guttmann gives the following table for the powder most commonly used:

	Saltpeter, Per Cent.	Sulphur, Per Cent.	Charcoal, Per Cent.
Germany	74	10	16
France	75	10	15
England	75	10	15
Holland	70	14	16
Italy	75	10	15
Austria	75	10	15
Russia	75	10	15
Switzerland	75	11	14
United States	75	10	15

The process of manufacture consists simply of mixing thoroughly the constituents, and of forming the mass into grains of different sizes, as required for different purposes.

The Raw Materials of Black Powder. The potassium nitrate (saltpeter) used in manufacture of black powder is either "natural" saltpeter or the so-called "conversion" saltpeter. "Natural" saltpeter is obtained by subjecting nitrogenous organic matter to decay in the presence of wood ashes. It has been manufactured in this manner from early times on a large scale in India. "Conversion" saltpeter is obtained by treating a solution of potassium chloride (Stassfurt salts) with the solution of a soluble nitrate, such as sodium nitrate from the Chili nitrate fields.

Natural saltpeter is preferred for powder making, since the conversion saltpeter frequently contains traces of potassium or sodium perchlorates, the presence of which makes the powder less uniform and less reliable. The better grades of sporting and military black powders are made from the natural saltpeter.

Charcoal which has been made by charring peeled, well-seasoned willow wood is preferred for black powder making, although many other kinds of wood, and even hemp, flax, and straw are used. For certain kinds of powder it is required that as much as possible of the volatile matter be driven off. For other kinds the wood is only partly carbonized, when the charcoal, instead of being black, has a red or brown appearance. These brown coals are used for making sporting powders and were formerly used exclusively in military powders for large caliber guns.

The sulphur used in black powder manufacture is ordinary sulphur as free as possible from impurities.

Process of Manufacture. The technical process of mixing these ingredients involves a number of separate operations as follows:

1. Pulverizing the raw materials.
2. Mixing the raw materials.
3. Compressing.
4. Graining.
5. Drying.
6. Dusting and sorting.
7. Polishing.
8. Blending.

The raw materials are first pulverized in revolving drums containing bronze balls. For this operation they are taken in pairs; that is saltpeter and sulphur; saltpeter and charcoal; charcoal and sulphur. The different pairs are then mixed in proper proportion and further ground in the ball-mill. In this condition the powder is known as "meal," and may be used without further treatment for making fireworks or fuses. It is not, however, in a form suitable for blasting or for use in firearms.

The grinding in the ball-mill serves merely as a preliminary mixing. To secure a more thorough incorporation of the raw materials, the meal is next ground in a mill provided with heavy edge-runners. This is a type of mill extensively used in many industries, and consists of two heavy, broad-edged wheels, connected by a short axle which is caused to revolve horizontally by an upright shaft. The two wheels or runners travel around a circular basin which contains the material to be ground, and which is subjected to a combined crushing and grinding action. This operation lasts about four hours. Before grinding under the edge-runners about 10 per cent of water is added to the powder to reduce the danger of explosion by friction. In spite of all precautions the mass frequently explodes and for this reason no person is allowed in the grinding room while the runners are in motion, the mills being started and stopped from a distance.

After the grinding is complete the mass is pressed into sheets, and the sheets subjected to further pressure and consolidation in a hydraulic press. The pressure employed in these hydraulic presses varies from 100 to 110 atmospheres, the powder remaining in the press for from one-half to two hours. Sporting powders are pressed so as to obtain a specific gravity of 1.7 or 1.8, while the specific gravity of blasting powders is only about 1.5.

The cakes are next broken up and the fragments passed through sieves of different mesh, which sort the material into grains of uniform sizes, the grains ranging from 0.3 to 1.8 millimeters in longest dimensions. The next step is to remove the greater part of the added water by means of dry air at a moderate temperature. When the moisture has been reduced so that the powder contains from 1.5 to 3 per cent, depending on the grade, it is again sifted to remove dust, which is returned to the grinding mill. The powder is then polished by rotating in wooden drums. This serves to rub off sharp corners. After a further sifting to remove dust, the powder is polished by shaking in the drum with a small quantity of graphite. Different grades of powder may be blended, as required, after which the finished product is packed for the market in air-tight packages.

Chemistry of Black Powder Explosions. The action of black powder as an explosive depends on the fact that on ignition the carbon and sulphur are rapidly burned at the expense of the oxygen of the potassium nitrate, whereby large volumes of gas are liberated.

The temperature of combustion being very high, the gas tends to increase enormously in volume; and if the space in which the combustion takes place is limited it exerts an enormous pressure and hence is able to rend obstructions, or propel shot. The ideal reaction of decomposition of black powder is:

$$2KNO_3+3C+S=K_2S+N_2+3CO_2.$$

But the products of decomposition vary greatly under different conditions. In general, black powder in decomposing gives off about 43 per cent of its weight of gaseous products and 57 per cent of solid products. Thus more then one-half of the products of decomposition contribute nothing directly to the force of explosion. This is one of the reasons why black powder is one of the least effective explosives in general use.

Mixtures Similar to Black Powder. Black powder may be regarded as the type of explosives which are essentially mixtures of a nitrate with easily oxidizable substances. Instead of potassium nitrate, the cheaper sodium nitrate might be used as a constituent of black powder, but this is not done on account of the greater hygroscopicity of the sodium salt. The non-hygroscopic character of potassium nitrate assures ordinary black powder a permanent place in the industry, as this property is indispensable for many purposes, such as in the manufacture of primers, fuses,

fireworks, etc., but where this is not essential, substitution of other nitrates may be made.

At the present time immense quantities of powders containing ammonium nitrate as base or as a prominent constituent are being made. Although hygroscopic, this salt has many properties which are very desirable from the standpoint of the user of explosives. Its low molecular weight gives it a relatively high oxidizing power per pound, and its products of decomposition being all gaseous, explosives containing it are consequently more powerful than those containing nitrates of metallic elements. Besides being more and more extensively used in industrial explosives it has been employed on a very large scale in the recent great war, especially in the form of a powder containing ammonium nitrate as oxygen carrier and dinitronaphthalene as oxidizable substance. At the present time the demand for ammonium nitrate is sufficient to absorb all the surplus nitric acid and ammonia the country can produce.

Ammonium nitrate has even been used to produce a powerful explosive known as *ammonal*. It consists of an intimate mixture of finely pulverized metallic aluminum and ammonium nitrate, which ideally decomposes according to the reaction

$$2Al+2NH_4NO_3=Al_2O_3+2N_2+2H_2O+H_2O.$$

This reaction develops great heat, which gives a correspondingly high pressure to the gaseous products. Unlike black powder, ammonal cannot be set off by a simple ignition, but must be exploded by a shock from the explosion of a primer charge of some fulminant, such as mercury fulminate.

Powders containing potassium chlorate as oxygen carrier are more powerful than those containing potassium or sodium nitrates, but as chlorate powders are more liable to be set off by friction or shock, they are more uncertain in their action and dangerous to handle. However, mixtures of potassium chlorate with oleaginous substances, such as nitro-toluols, ricinus oil, paraffin, etc., have been found satisfactory in use. An explosive of this type, known as *cheddite* has been manufactured by the French powder monopoly and other concerns. Owing to the fact that chlorate mixtures give off chlorine compounds on decomposition, they are little suited to use in underground work.

The objections to chlorate mixtures on the score of sensitiveness do not seem to apply to the same extent to mixtures with ammonium perchlorate as oxidizing base, and when this substance becomes available in large quantity at a fair price, it will undoubtedly figure largely in the explosives industry.

Nitrocellulose. Nitrocellulose, or more properly speaking, cellulose nitrate, is now the chief material used in the manufacture of military and sporting powders throughout the world. In conjunction with camphor and other substances it is also used in making celluloid.

Nitrocellulose is not a nitro-compound, as chemists understand that term, but is a true nitrate in which the hydroxyl groups of the cellulose molecules have been replaced by the nitrate radicle (NO_3). The inaccurate designation, nitrocellulose, which was given to the substance by its early investigators, has, however, been so long in use that it is not likely to be supplanted by the more correct term. Nitrocellulose is manufactured by subjecting cellulose to the action of strong nitric acid under certain definite conditions.

Raw Materials of Nitrocellulose Manufacture. The raw materials used in making nitrocellulose are cellulose (in the form of wood pulp, tissue paper, cotton wool, or cotton waste from spinning mills) and sulphuric and nitric acids. For making nitrocellulose to be used in the cheaper grades of celluloid and in certain cheap commercial explosives wood pulp or paper may be used. For making smokeless powder for military use, only the best and purest forms of cellulose can be employed, such as cleaned and bleached cotton wool and spinning mill waste. The so-called delint cotton is mostly employed. A satisfactory smokeless powder for immediate use can be made from well-purified sulphite paper pulp, to which the Teutonic Allies have been forced to resort by the scarcity of cotton.

Preliminary Treatment of the Cellulose. The cotton wool or waste must first be deprived of impurities such as oil, fat, or dirt. This is done by boiling with dilute alkali. This treatment is next followed by light bleaching by means of calcium hypochlorite, for the purpose of removing lignine substances that form unstable nitrates which would impair the stability of the product. Too vigorous a bleaching is to be avoided, as otherwise hydrocellulose or oxycellulose would result, and give rise to unstable nitrates and low yields.

Before the bleached cotton is subjected to nitration it is dried so as to reduce its moisture content below 1 per cent. For this result exposure to a temperature of 105° C. is usually necessary.

The Process of Nitration. Nitrocellulose is not a definite compound of invariable composition like calcium nitrate. The cellulose molecule can be made to take up about 14 per cent of nitrogen, but below this maximum, products of any degree of nitration can be obtained. Products of similar nitrogen content prepared under closely similar conditions may differ widely in properties. For this reason practical operations have to be carried on with great attention to detail.

The process of manufacture in outline consists in dipping the cotton into a mixture of strong nitric and sulphuric acids, allowing to stand for a short time, and then removing the acid and purifying the nitrocellulose. The degree of nitration and the properties of the product are dependent on the temperature of nitration, duration of the action of the acids, ratio of the mass of cotton to the mass of acids, and relative proportions of sulphuric acid, nitric acid, and water in the acid mixture. A

variation in any one of these factors affects the degree of nitration and the quality of the product. The reaction whereby nitrocellulose is formed from cellulose and nitric acid is:

$$C_{24}H_{40}O_{20} + nHNO_3 = C_{24}H_{40-n}O_{20}(NO_2).$$

In this equation n represents any number between 1 and 11. The sulphuric acid, which constitutes three-fifths of the acid mixture, takes no direct part in this reaction.

Pyro. Nitrocellulose of from 12.50 to 12.70 per cent of nitrogen is called pyrocellulose, or simply pyro, and is the material from which smokeless powder for cannon is made. A property of pyro is that it is soluble in a mixture of ether and alcohol, by which means it can be worked into a dough, and thus formed into any desired shape. Specifications under which smokeless powders for cannon are made call for pyro with 12.60 per cent plus or minus 0.1 per cent of nitrogen, and solubility in ether-alcohol of 99 per cent. To produce a nitrocellulose of this sort it is necessary to use a nitrating mixture with a total acidity of about 85 per cent, and about 15 per cent water. The proportions of sulphuric and nitric acids in the nitrating acid may vary within rather wide limits, but the best manufacturing practice is to keep the proportion of nitric acid low. A typical pyro mixed acid would have the following composition:

	Per Cent.
H_2SO_4	63.0
HNO_3	19.5
N_2O_4	2.5
H_2O	15.0

This mixture would have an available acidity of 84.21 per cent, the nitrating value of the N_2O_4 being half its equivalent of HNO_3.

Military Gun Cotton. Another sort of nitrocellulose for military and sporting powders is known as military gun cotton, or M.G.C. Specifications for this product require that it shall have from 13.00 to 13.30 per cent of nitrogen and a solubility not exceeding 13 per cent in ether-alcohol. M.G.C. is used chiefly in ammunition for small arms and in contact mines. It is made with a nitrating acid having total acidity of about 90 per cent, a typical mixed acid having the composition:

	Per Cent.
H_2SO_4	68.50
HNO_3	20.65
N_2O_4	.85
H_2O	10.00

The initial temperature of nitrating for M.G.C. is 25° C. plus or minus 1°. If this temperature is not arranged for, the limits of solubility may be

exceeded. The time of nitration is the same as for pyro. For working M.G.C. into the desired forms, acetone, amyl acetate or nitroglycerine may be used as solvents to confer the necessary plasticity.

The strength of the nitrating acid used in making nitrocellulose for smokeless powder will vary slightly from the above-mentioned mixtures according to climatic conditions, a stronger acid being required in cold than is required in warm seasons.

Methods of Nitrating Cellulose. Many different methods of nitrating cellulose have been proposed and used. The primitive method was to employ earthenware or iron pots of small capacity as nitrating vessels. Pot nitration is generally slow and expensive. Within recent time the most general practice was to conduct the nitration in an iron centrifuge capable of holding a charge of about 16 pounds of raw cotton. The mixed acid of the desired strength, previously warmed to the requisite temperature, is run into the bowl of the centrifuge, and the raw cotton, which has been dried to less than 1 per cent of moisture, is submerged in the acid by means of pitchforks. The bowl of the centrifuge is then covered and allowed to stand undisturbed for the required length of time, the fumes given off during the reaction being led away through a wide duct. At the end of the period of digestion the spent acid is withdrawn through a pipe leading from the bottom of the bowl, and as much as possible of the acid still adhering to the nitrocellulose is removed by rotating the bowl of the centrifuge at a high speed. The nitrocellulose is then removed from the bowl with pitchforks and promptly "drowned" in a large tank containing water, or in a large flume through which running water washes it into a dump tank, whence it is removed to the boiling tube.

The initial nitrating temperature for pyro is 30° C. plus or minus 2°, and the reaction is complete in ten to thirty minutes, depending on the type of nitrating equipment used. After the raw cotton has been submerged in the acid and the reaction commences the temperature will rise 8° to 10°. The porportions by weight of raw cotton to mixed acid in nitrating for pyro is 1 to 40.

The Displacement Process of Nitration. A more recent process of nitrating, one which in many respects is more advantageous than nitrating in centrifuges, is the displacement process. Fig. 364 is a schematic diagram showing in principle the construction of an apparatus of this type. The circular stoneware vessel *A*, having a conical depression at the bottom, from which leads the pipe *B*, is provided with a perforated stone false bottom *F*, on which the cotton to be nitrated is placed. By a suitable arrangement of pipes, mixed acid is admitted into the vessel until the cotton is covered with it. The cotton is kept submerged beneath the acid by the weight of the movable cover *D*, which is also perforated. Over the opening of *B* there is a fine sieve to catch particles which pass through the perforated bottom of the vessel. After the apparatus has been filled with cotton and acid and the movable cover is in position, a small quantity of

water is poured over the surface for the purpose of preventing the escape of fumes. This water comes in contact with the acid only at the edges and in the perforations of *D*. Under these circumstances the acid and water remain in sharply separated layers.

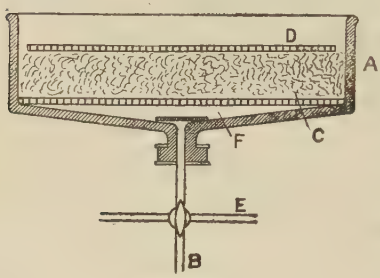

FIG. 364.

The vessel and its contents are now left to themselves for about an hour, when the stop-cock is opened and the acid allowed to flow off slowly by gravity, water being led in at the top as fast as the acid flows away at the bottom, until the acid has been completely displaced from the apparatus. No mixing of acid and water, and no noteworthy rise in temperature occurs during the displacement. After the preliminary washing in the same vessel, the nitrated cotton is removed and purified as usual. The displacement process of nitrating requires more time than the centrifugal process, but it has distinctive advantages in the absence of fumes, less labor required, and greatly diminished expense for repairs. The displacement process is the one chiefly used in manufacturing nitrocellulose for the English government and by the U. S. Army Ordnance Department. Its advantages are disputed by some authorities.

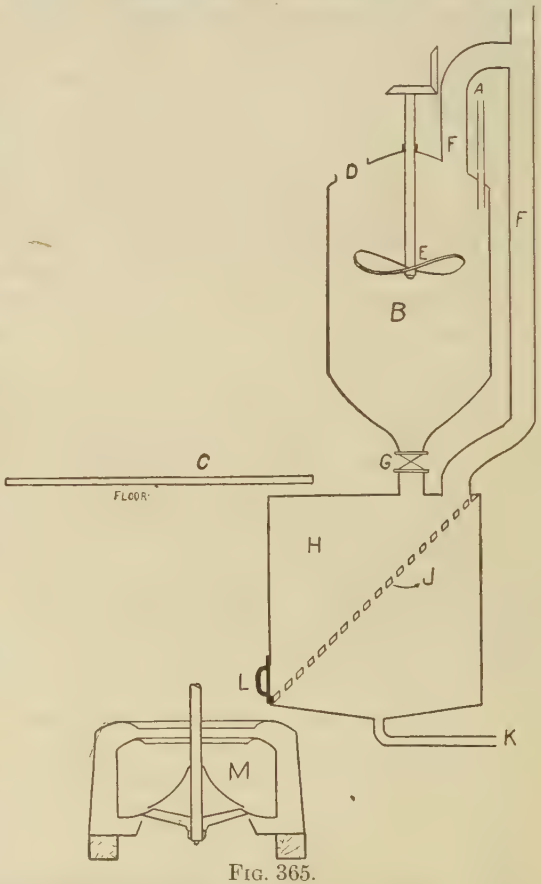

FIG. 365.

Mechanical Dipping Process. The enormous demand created by the great war for nitrocellulose for military purposes has stimulated development of methods of nitration having in view greater output, reduction in the amount of hand labor required, as well as increased comfort to the operatives through better control of the acid fumes given off during the process.

One such device is illustrated schematically in Fig. 365. Mixed acid previously brought to the required temperature is led through pipe *A* into the nitrating vessel *B*. The operator, standing on platform *C*, introduces the dried cotton through the opening *D*; the agitator *E* submerges it in the acid, the fumes given off being led away through the duct *F*. After the lapse of the proper length of time the charge is dumped through the quick-opening valve *G* into the receiver *H*; the spent acid drains from the mass through the sloping perforated diaphragm *J* and flows away through *K*. The nitrocellulose is raked through the port *L* into the bottom discharging centrifugal *M*, where the remaining spent acid is removed by centrifugal force, after which the product is dropped into the flume, which carries it to the boiling tubs. In other systems the vessel *H* is dispensed with, the charge going direct to the centrifugal. With an installation such as this it is possible to nitrate a charge of 24 pounds of raw cotton every ten minutes with an almost entire absence of annoying fumes.

Nitrocellulose for use in making celluloid and other plastics contains from 8 to 12 per cent of nitrogen and its manufacture requires other conditions than those obtaining in the manufacture of nitrocellulose for explosives.

Nitrocellulose for military purposes, being manufactured under close official supervision, is naturally purified with greater care and at greater expense than nitrocellulose for industrial use.

Purifying the Nitrocellulose. In the process of nitration there are formed small amounts of sulphuric esters of cellulose, and free acid is drawn by capillary action into the canal which exists in the central portion of the cotton fiber. This free acid must be quite thoroughly removed and the sulphuric esters saponified, otherwise the nitrocellulose will in a longer or shorter time become unstable and liable to spontaneous decomposition, with possible disastrous results at some subsequent period of use of storage. After being thrown out of the nitrating vessel into the drowning water, the nitrocellulose is conveyed to large wooden boiling tubs, where it is boiled for forty hours, with four changes of water. This removes practically all of the free acid, but to remove all traces of acid and to insure the complete breaking up of all sulphuric acid compounds it is necessary to reduce the nitrocellulose to a fine state of division. This is accomplished in a beater, in all respects similar to the beating or pulping engine commonly used in the paper industry. The beating process, by breaking up the cotton fiber, allows water to have access to all parts of the interior canal. A little soda is added in sufficient amount to keep the contents of the beater alkaline. After beating, the nitrocellulose is transferred to other large wooden tubs known as " poachers," where it is boiled and mechanically agitated for a period of twelve hours, with six changes of water, and then given ten cold washings with cold water. At the end of this treatment " pyro " should stand a " heat test " of not less than thirty-

five minutes at 65° C.; M.G.C. should give a heat test of ten minutes at 70° C. A heat test is made by exposing a strip of K I starch paper in a test tube containing a definite amount of the nitrocellulose heated to the temperatures named above, and noting the time required to produce a discoloration of the paper.

After purification is complete the nitrocellulose is freed from excess of water by means of a hydro-extractor. Owing to the ease with which it may be ignited by a chance spark, nitrocellulose is always stored and transported in a moist condition, the I.C.C. regulations prescribing a minimum of 20 per cent water. Nitrocellulose with not more than 15 per cent of water, though relatively difficult to ignite, can be detonated with mercury fulminate primer, and in this form is used in contact mines.

Regeneration of Acid. The acid which is separated from the nitrocellulose after nitration is known as "spent acid"; it is naturally weaker in strength than the original nitrating acid, owing to fixation of NO_3 and formation of water in the reaction. By adding to it additional nitric acid in the form of "fortifying acid," it may be used over again. A certain amount of both sulphuric and nitric acids is necessarily lost in the drowning water. In practice about 0.8 pound of sulphuric acid and 1.7 pounds of nitric acid are consumed or lost for each pound of cotton nitrated.

Nitro-starch. Nitro-starch, or more correctly starch nitrate, is manufactured to some extent for use in blasting explosives. Cassava starch is the most suitable for this purpose. The process of manufacture differs somewhat from the manufacture of nitrocellulose, the points of difference being in the use of stronger acid and appropriate means of mixing the starch with the acid, and separating the product therefrom. The advantage of using starch over cotton is its comparative cheapness, although the difficulty of purifying the nitrated product has prevented it from being used in the manufacture of smokeless powders.

Smokeless Powder. The base of all smokeless powder is nitrocellulose. Powder for cannon is made of pyro, and of M.G.C. for small arms. The reason for this choice is that since it contains less nitrogen as NO_3, pyro is less erosive on the bore of the gun than M.G.C., erosion being a serious matter in limiting the life of a large and costly weapon. Also, by reason of its greater solubility, pyro can be worked into a more satisfactory colloid than M.G.C.

In manufacturing cannon powder, the pyro, as it comes from the hydro-extractors at the close of the purification process, is weighed out in portions or charges to contain 40 pounds dry weight. This charge is placed in a hydraulic press and alcohol of 92.3 per cent by weight forced through in order to displace all water and leave 14 pounds of alcohol in the resulting block. The block is then broken up, and the screened product placed in a Day or Werner-Pfleiderer mixer and incorporated with an amount of ether equal to twice the weight of alcohol in the pyro. The action of the ether-alcohol mixture produces a semi-solution or colloidal mass. After

mixing with ether the colloided pyro is blocked in a hydraulic press, and further kneaded and mixed by being forced through a straining press, and finally reblocked. These manipulations are for the purpose of removing uncolloided material and producing a colloid of smooth, even texture. The blocked pyro is then run through a "graining press," which forms it into long rods having one or more axial perforations; these rods are passed through a cutting machine to produce grains of proper length. The dimensions of the grain are dependent on the size and caliber of the gun in which it is to be used; and hence a "grain" of powder may have any dimensions up to a length of 2 inches and a diameter of $\frac{7}{8}$ of an inch.

After leaving the graining press the powder is taken to bins, in which gentle heat is applied to expel as much as possible of the ether-alcohol (which is condensed and recovered). After leaving the "recovery bins" the powder still retains a large proportion of solvent, and to reduce this to the proper limits the powder is placed in an "air dry house" and subjected to dry heat at 55° C. for several weeks, or months, as conditions may require. In order to save time, field gun powders may be "water dried," that is, soaked in warm water to extract the excess of solvent, and then air-dried. By this means it is possible to produce a usable powder in three weeks from the date of nitration.

In making powder for small arms, the M.G.C. is colloided with acetone or amyl acetate, with addition of nitroglycerine to increase the strength. The colloid is rolled into sheets, cut into small squares, which are then graphited in a tumbling barrel, and dried.

In use the powder is suitably packed in a cartridge or case and ignited by means of a mercury fulminate primer, which acts on a priming charge of ordinary black powder; this produces a flame which sets off the powder charge.

Smokeless powder derives its name from the fact that in comparison with black powder it gives off very little smoke.

Stabilizers. Smokeless powder, even when made from nitrocellulose of the highest purity, is apt to undergo a progressive though very slow decomposition. This deterioration consists in a saponification of the cellulose nitrate, with setting free of N_2O_4, which acts catalytically in producing further decomposition, which may proceed to the extent of causing spontaneous combustion. To prevent or delay this occurrence about .4 per cent of diphenylamine or other substance capable of neutralizing N_2O_4 is incorporated in the powder, being added to the ether used for colloiding.

Cordite. At the beginning of the recent great war the smokeless powder preferred by the British military services was made of nitrocellulose worked into a colloid with 20 to 40 per cent of nitroglycerine and a small amount of acetone. Smokeless powder with nitroglycerine base is more powerful and can be made to give more uniform ballistic results than the straight nitrocellulose powder. However, the temperature of explosion of

cordite is higher, and the hotter gases have a more erosive action on the bore of the gun. This is serious matter under present conditions of warfare, and hence the use of cordite is being abandoned to a large extent. All other nations, including the United States, use straight nitrocellulose powder.

Picric Acid. Picric acid, or trinitrophenol—$C_6H_2(NO_2)3OH$—belongs to a group of substances technically known as "high explosives" or explosives which develop their explosive effect at a much more rapid rate than smokeless or black powders, and hence are used where a shattering effect of great violence is required. In artillery operations smokeless powder is used to fire the projectile from the gun; for certain military purposes the projectile is a hollow steel shell, the cavity of which contains picric acid or T.N.T. (see below). When the shell strikes the mark the charge of picric acid is set off, and rending the shell throws splinters of metal about the neighborhood as well as demolishing objects in the vicinity by the force of the explosion itself. Although a very powerful explosive, picric acid cannot be readily set off by simple ignition, like smokeless or black powder, but must be detonated by means of a primer of mercury fulminate contained in the shell.

Picric acid is made by nitrating phenol. Specifications for picric acid require it to have a melting-point of at least 120° C., which makes it necessary to use high-grade phenol (m.p. 40° C.). The phenol is melted in the drum in which it is received at the factory and blown into an iron sulphonating kettle where it is sulphonated with 93 per cent H_2SO_4 at a temperature of about 100° C., the heating being continued until no free phenol separates when diluted with water. The time required for sulphonation is about ten hours and the temperature must not be allowed to rise above 105°. When sulphonation is complete, the product is diluted with an equal quantity of water and pumped into a storage tank lined with acid-proof brick, which is provided with an agitator. Enough of the sulphonate is run into the nitrator to engage the lower blades of the agitator, whereupon nitric acid (70 per cent) is run in rapidly to bring the temperature to 70° C., after which nitric acid and sulphonate are run in together at a rate sufficient to bring the temperature in half an hour to 110°, this temperature being maintained for $5\frac{1}{2}$ hours, when the mixture is allowed to cool to 55°. The total time required for nitration depends on the size of the units employed. After nitration is complete the spent acid, which contains about 2 per cent HNO_3, is drained off, the picric acid washed several times with cold water, centrifuged in cloth-lined wringers and removed to dry houses, where the moisture is reduced to the limits prescribed by the Interstate Commerce Commission for the transportation of this substance.

Picric acid has not come into use as an industrial explosive, on account of its comparatively high cost.

On account of its acid character, picric acid forms salts with nearly

all metals, and all of its salts, with the exception of ammonium picrate, are more sensitive to shock and friction than the acid itself. Contamination of the acid with its salts is therefore to be avoided.

Trinitrotoluol, $C_7H_5(NO_2)_3$, or T.N.T. This product, known commercially as T.N.T., is obtained by nitrating toluol. Trinitrotoluol, like picric acid, is classed as a high explosive and is extensively used in military operations as a bursting charge for large-caliber shells, and for the war heads of submarine torpedoes. It is also used along with nitroglycerine in various grades of dynamite.

Although somewhat less powerful as an explosive than picric acid, T.N.T. is a much more satisfactory substance to deal with on account of its low melting-point (80° C.), which allows it to be readily melted and poured, and on account of its comparative insensitiveness to shock, which makes it relatively safe to handle. Not possessing any acid properties it forms no sensitive salts, as is the case with picric acid, and thus it possesses an additional factor of safety.

Toluene suitable for nitration should have a boiling-point of about 110° C., not beginning to distill under 108.5° and going over entirely under 111°. Specifications for T.N.T. usually call for a melting-point of around 75.5° and nitrogen content of not less than 18 per cent. "Refined T.N.T.," with m.p. of 80° is sometimes demanded, and may be made by recrystallizing the 75° grade from 100 per cent HSO_4, or by simple washing with 5% Na_2SO_3 solution.

In the manufacture of T.N.T. there is a choice of four different methods, viz.:

1. Three stage; involving the preparation of mono-nitrotoluene (M.N.T.) which is then separately nitrated to dinitrotoluene (D.N.T.) which by a third operation is nitrated to T.N.T.
2. Two stage; producing first M.N.T. and then T.N.T.
3. Two stage; producing first D.N.T. and then T.N.T.
4. One stage; producing T.N.T. in one operation.

The choice of method depends on circumstances and whether the manufacturer has any use for the intermediate products, as such, for other purposes. Where T.N.T. is the sole product desired methods two and four are principally used, method two seemingly offering the most advantage.

In making T.N.T. in a one-stage nitration 4500 pounds of mixed acid having the composition:

	Per Cent.
H_2SO_4	76.0
HNO_3	22.5
NO_2	0.6
H_2O	0.9

is run into 1200 pounds to toluol. The temperature at the start is 35°, being slowly raised in four hours to 110°, where it is held until a melting-point test shows that satisfactory nitration is attained.

The yield may be increased and the melting-point raised by cooling to 90° after the fifth hour of heating and adding fresh mixed acid composed of 1000 pounds each of oleum and the above-mixed acid.

In a two-stage process, M.N.T. is obtained by nitrating 3350 pounds of toluol with 7700 pounds of a mixed acid containing:

	Per Cent.
H_2SO_4	55
HNO_3	31
H_2O	14

The temperature is kept under 50° until all the acid has been added, when it is raised to 70° and held there for two hours. The resulting M.N.T. is separated from the acid, and nitrated to T.N.T. with a mixed acid containing:

	Per Cent.
H_2SO_4	58.50
HNO_3	40.50
H_2O	1.00

The M.N.T. is first dissolved in $2\frac{1}{2}$ times its weight of 100 per cent H_2SO_4 and run into the mixed acid, the temperature not being allowed to exceed 115°. The spent acid from this operation is used in making M.N.T.

The adaptability of T.N.T. for use as a component of blasting explosives assures it a permanent place in the industry, especially in view of the steadily advancing cost of nitroglycerine and the expansion of the by-product coke industry, which is making available larger quantities of toluol. Explosion of T.N.T. may be brought about by means of a primer of mercury fulminate.

Other Nitro-compounds used as Explosives. Dinitrobenzol and trinitrobenzol have been used to some extent as constituents of commercial explosives, but not extensively in this country. The nitration products of xylol and naphthalene are coming into considerable prominence, as their use affords the most convenient outlet for the excess production of these hydro-carbons. "Nysol," obtained by nitrating a solution of naphthalene in xylol, is used in the manufacture of low-freezing dynamites (see below).

Titranitroaniline (T.N.A.), made by nitrating aniline, is used in the manufacture of detonators and primers.

Nitroglycerine and Dynamite. Explosives composed wholly or in part of nitroglycerine and closely related substances are at the present time the most important of industrial explosives.

Nitroglycerine is formed from nitric acid and glycerine in accordance with the following reaction.

$$C_3H_5(OH)_3+3HNO_3=C_3H_5(NO_3)_3+3H_2O.$$

Nitroglycerine, like the analogous product of the interaction of nitric acid and cellulose, is a true nitrate and not a nitro-compound. The term

" nitroglycerine " is therefore a misnomer, which, however, is apparently too well intrenched in common usage to make way for the more appropriate name.

Raw Materials of Nitroglycerine Manufacture. The materials used in making nitroglycerine are nitric acid, sulphuric acid, and glycerine. The reason for employing sulphuric acid here, as in the case of nitrocellulose manufacture, is to take up the water formed in the reaction, thereby keeping the nitric acid up to its full strength. The glycerine employed is the ordinary glycerine of commerce, obtained as a by-product in the saponification of fats. It has a specific gravity of 1.262, corresponding to 99 per cent of glycerine and 1 per cent water.

Process of Manufacture. The process of manufacture consists simply in adding the glycerine to the mixed acids (observing suitable precautions), separating the glycerine nitrate from the acid mixture, and purifying it. The methods used in practice for carrying out this simple reaction, however, are very diverse, and for full details thereon reference must be had to larger treatises such as Guttmann's " Manufacture of Explosives," and recent patent specifications.

In principle the arrangement of the apparatus for making nitroglycerine may be seen from the accompanying diagram, Fig. 366. In this diagram *a* is the nitrating vessel in which the glycerine is brought into contact with the mixed acids. It is provided with a thermometer, a coil for cooling and a device for stirring the mixture. This device may consist of either a mechanical stirrer, or an inlet for compressed air. *b* is a tank into which the contents of the nitrating vessel are discharged and allowed to remain until the nitroglycerine has separated from the acids. Being of a lighter specific gravity than the mixed acids, the nitroglycerine collects at the top. *c* is a vessel into which the separated nitroglycerine is drawn and given the first washing to remove the adhering acids. *d* is a safety tank full of water into which the contents of *a* or *b* may be dumped whenever it appears to the workmen in charge that the nitroglycerine contained in these vessels is about to decompose with violence. The probability of such a contingency is observed by a sudden rise in temperature and the appearance of dense red fumes. When the nitrating mixture gives such indications prompt action is necessary to save life and property.

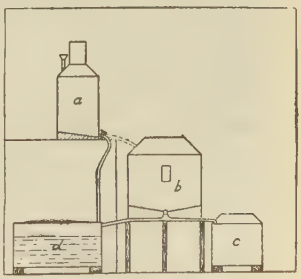

FIG. 366.

According to the equation given above 2.15 parts of nitric acid (95 per cent strength) is sufficient for complete nitration of the glycerine. As, however, complete nitration is not attained except in the presence of an excess of nitric acid, and not then except in the presence of much sulphuric acid, it is usual to employ the following proportions: glycerine, 1 part;

nitric acid 2.8 to 3 parts, and sulphuric acid 4.6 to 4.8 parts. The yield of nitroglycerine may be increased by adding more nitric acid, but in general the theoretical yield is never reached. According to the relative prices of glycerine and nitric acid the proportions of these materials may be varied to conform to the limits of economical production.

Fig. 366*a* shows the nitrator, and Fig. 367 the washing vessels of a small plant for nitrating glycerine. This plant will use for one charge 4000

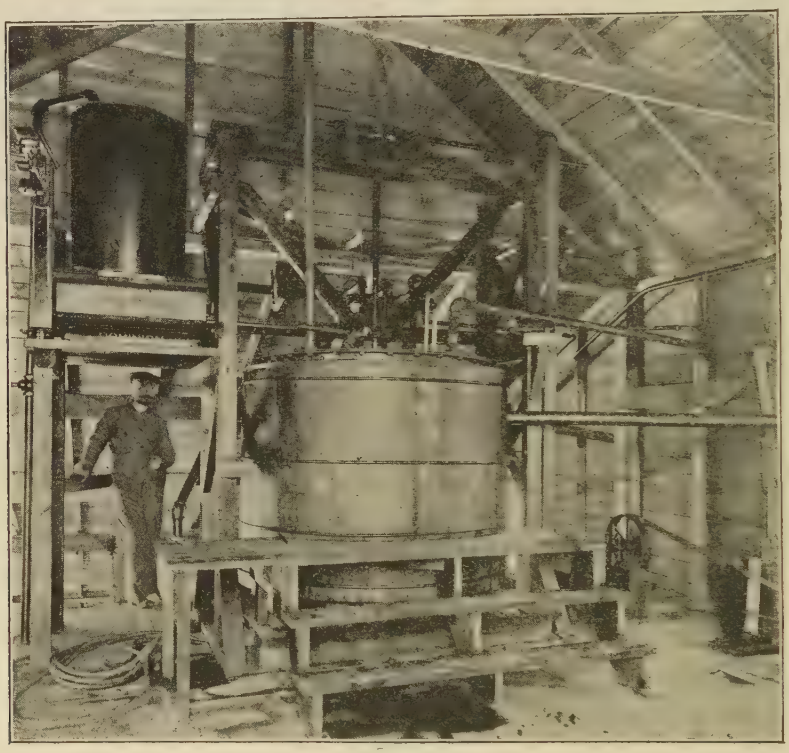

Fig. 366*a*.

pounds of a mixed acid consisting of: 35.5 per cent of nitric acid; 62 per cent sulphuric acid; 2.5 per cent of water; into which is run 635 pounds of glycerine, the temperature during this operation being maintained at about 65° F. The run should be completed in less than forty minutes. Under the given conditions, these materials will yield 1400 pounds of nitroglycerine.

The nitroglycerine after separation from the acid is first washed twice with small amounts of water, using compressed air for the mixing. It is then washed with a weak solution (not exceeding 1 per cent) of sodium carbonate, this salt being added to the wash a little at a time. The object of using the sodium carbonate is to neutralize the acid which may not have been removed by the wash water. This treatment is then followed

by a thorough washing with pure water at a temperature below 90° F. to remove the alkali, no trace of which should remain. The point at which the washing may be regarded as complete is recognized by the potassium-iodide-starch test, as described under nitrocellulose. In this test no iodine should be liberated within twenty minutes at a tempera-

Fig. 367.

ture of 170° F., otherwise the washing must be continued until a satisfactory test has been obtained.

Dynamite. Nitroglycerine is a heavy oily liquid and in this form has but a limited applicability. For convenience in use it must be put into a form wherein it may be easily handled. This is done by causing it to be absorbed by various porous bodies, such as infusorial earth, or kieselguhr, which can be made to absorb three times its weight of nitroglycerine. Such a mixture of nitroglycerine and kieselguhr forms an earthy, friable mass, which can be loaded into paraffined paper cartridges and has been sold under the name of 75 per cent dynamite, or No. 1 giant powder. This is the original dynamite as manufactured by its inventor, Nobel.

A disadvantage of kieselguhr dynamite, which is now obsolete, is that it contains 25 per cent or more of its weight of inert matter, whereby its strength as an explosive is correspondingly reduced. On this account the original dynamite has been improved by the choice of other absorbent

agents. The dynamite now mostly used consists of 15 per cent of wood pulp (sometimes partly nitrated), 33 per cent of nitroglycerine and 55 per per cent of sodium nitrate or ammonium nitrate. The wood pulp serves to absorb the nitroglycerine, but this, as in the case of kieselguhr, means the introduction of an inert material into the explosive. The wood pulp, however, unlike the kieselguhr, contains carbon and hydrogen, which can combine explosively with oxygen under appropriate conditions. These conditions are supplied by the presence of sodium nitrate, or, better, ammonium nitrate, which here serves the same purpose of oxygen carrier as does potassium nitrate in black powder.

Dynamites are generally classified according to the amount of nitroglycerine content. Thus a 50 per cent dynamite contains 50 per cent nitroglycerine.

Gelatine Dynamite. Nitroglycerine has the property of dissolving nitrocellulose to a limited extent. A mixture of approximately 9 parts of nitroglycerine and 1 part of nitrocellulose forms a clear, jelly-like mass containing no inert matter, which constitutes a powerful explosive. The name gelatine dynamite is applied to this product on account of its jelly-like consistency, and not because it contains gelatine.

Low-freezing Dynamites. An undesirable property of nitroglycerine, whether alone or mixed with inert substances, is that it solidifies at comparatively mild temperatures. When so frozen it is less sensitive to shock and is less apt to be completely exploded when set off in a blast. For this reason frozen dynamite must be thawed out before use. Much attention has been devoted to attempts to obviate this inconvenience and in recent times these efforts have resulted in various new modifications of dynamite. The most direct treatment is to add some substance, such as mononitrobenzene, dinitrobenzene, nysol, etc., to the nitroglycerine with the object of reducing its freezing-point. Satisfactory results have also been obtained by the manufacture of other nitration products of glycerine. Of these may be mentioned the following:

Dinitroglycerine. This is made by adding 10 parts of glycerine (specific gravity, 1.262), with cooling, to 33 parts of nitric acid (specific gravity, 1.50). The dinitroglycerine is recovered from this mixture by diluting with water. While the freezing-point of nitroglycerine is 11° C., that of dinitroglycerine is −57° C. In possessing such a low-freezing point, dinitroglycerine has a distinct advantage over trinitroglycerine, although it is not without certain other disadvantages, besides being somewhat less powerful as an explosive.

Tetranitrodiglycerine. When glycerine is boiled for some time there is formed a substance known as diglycerine, which consists of two molecules of glycerine. When nitrated the resulting tetranitrate also has a low freezing-point. Nitration of a mixture of glycerine and diglycerine gives a means of making low-freezing dynamites.

Dinitromonochlorhydrin. This is obtained by nitrating monochlor-

hydrin, $C_3H_5(OH)_2Cl$. An addition of 30 per cent of dinitromonochlorhydrin to nitroglycerine makes the resulting mixture practically unfreezable. On account of the presence of chlorine in this substance explosives containing it cannot be used in mines, or other closed spaces, as it makes the air irrespirable.

Another substance which has been used in the manufacture of low-freezing dynamites is dinitroacetin.

Safety Powders or Permissibles. The necessity of adapting the composition of an explosive to the conditions under which it is to be used is exemplified in coal mining, where there is the ever present danger of igniting the dreaded "fire damp."

An explosive mixture of air and methane will ignite only when locally heated above a certain critical temperature for a sufficient length of time, or when exposed to an open flame of sufficient duration. To be used with safety in a gassy coal mine a blasting explosive must not give rise to either of these conditions, and the problem of the manufacture of permissible explosives is to adjust the composition of the powder so that the heat of explosion shall be as low as practicable and to diminish the amount of flame. This is accomplished in various ways, as by the addition of inert matter, which becomes heated in the explosion, thus absorbing heat units which would otherwise serve to raise the temperature above the safe limits. Inorganic salts (such as magnesium sulphate) containing water of crystallization come under this category, and are quite effective on account of the amount of heat absorbed by the volatilization of the water of crystallization. Another means to the same end is to employ an excess of wood pulp in the powder; the limited amount of available oxygen as NO_3 in the powder causes the production of CO rather than CO_2 from the carbon of the cellulose, with lessened production of heat in the reaction; powders containing 80 per cent of ammonium nitrate, with small quantities of rosin, wood pulp, and nitroglycerine make good safety explosives for coal mines.

The liability of a blasting powder to ignite fire damp or cause an explosion of coal dust is ascertained by firing a standard charge of the powder in a tunnel in which the conditions as to gas or dust existing in a coal mine are simulated. Tests of this character are carried out by the Bureau of Mines at Pittsburg, and powders meeting the requirements are allowed to be sold as "permissible explosives."

"Railroad or Ditch Powder." For loosening masses of earth, as in railroad excavation or farm ditching, a low-grade dynamite is extensively used containing about 10 per cent of nitroglycerine, absorbed in a finely ground mixture of coal, sulphur, sodium nitrate, rosin, or similar materials. A powder of this character has a comparatively slow rate of burning which adapts it for upheaving soft materials, where a high-grade dynamite would merely blow out a small crater—another example of adapting the composition of an explosive to the effect desired.

Fulminants, Primers, or Detonators. Explosives may be divided into two general classes according to the means required to set them off, or bring about their decomposition with explosive effect. The first class includes those which are set off by simple ignition. To this class belong black powder and nitrocellulose. When a lighted match is applied to black powder, the part first heated begins to burn with great rapidity, the combustion being supported by the materials contained in the explosive itself, i.e., there is induced a chemical action between the potassium nitrate on the one hand and the carbon and sulphur on the other. The resulting process of combustion is rapidly propagated throughout the mass and there is suddenly produced a large volume of hot gas with an enormous expansive force. Comparatively speaking, however, the wave of combustion in black powder travels at a low speed. The force of the explosion, therefore, develops slowly and its rate of development is easily capable of measurement.

The second class of explosives here considered are those whose explosive effects are not developed by mere ignition. Dynamite, smokeless powder, and picric acid, for example, when set on fire under certain conditions merely burn without necessarily producing an explosive effect. If, however, picric acid or nitroglycerine (and under certain conditions, nitrocellulose also) be confined in a small space and struck a sharp blow, there is set up an explosive wave of decomposition, distinct from the wave of combustion, the difference between the two being that the former is propagated with practically immeasurable velocity. In order to bring about the maximum effect of such an explosive, it is necessary to induce an explosive wave in its mass, and this in practice is accomplished by the use of a " priming charge," consisting of a small amount of some explosive which decomposes with extraordinary velocity. Such primers are the salts of fulminic acid, the most important being mercury fulminate. So great is the rate of decomposition of this substance when heated or struck that the expansion of the evolved gas has the effect of a blow delivered by a mass moving at a velocity infinitely great. The shock so produced against the adjacent mass of picric acid or similar body is translated into a wave of decomposition, which instantaneously transforms it into gaseous products.

Mercury fulminate can be made to set off black powder and all other explosive mixtures. It is used in the form of caps or detonators in practically every instance where an explosion is to be brought about, whether for industrial, sporting, or military purposes. All shells used in modern warfare carry special detonators of mercury fulminate for setting off their bursting charges. In igniting charges of smokeless powder in cannon, the fulminate primers first acts on a charge of black powder, the flame of which ignites the powder grains. In blasting operations the charge of dynamite, for instance, may be ignited by a fuse, which is a long string made of cotton impregnated with finely ground black powder. When one end of the fuse is ignited by a match the fire travels slowly down the string until it reaches the primer, giving the operators an opportunity to with-

draw to a place of safety. A more convenient way of firing blasts, however, is to detonate the primers by means of an electrically heated wire. In this way any number of charges may be fired simultaneously.

Mercury fulminate is made by dissolving mercury in nitric acid in the presence of alcohol. Its manufacture and handling are very dangerous. A good substitute for mercury fulminate in primers is a mixture of potassium chlorate with powdered glass and antimony trisulphide or various metallic thiosulphates. Such priming mixtures are safer to handle than the fulminate and for this reason are growing in favor.

Another good priming charge has the composition:

	Per Cent.
Chlorate of potassium	48
Sulphide of antimony	30
Powdered sulphur	22

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CHAPTER XLVII

LEATHER

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Pelts of animals left in a moist condition soon putrefy; if dried, they become hard and horny. These objectionable conditions are overcome by what is known as tanning, a process which renders the putrescible animal matter less perishable and at the same time soft and flexible enough to answer its intended purpose. In view of the great variety of leathers, ranging from heavy sole leather to light kid, there are likewise wide divergences in the processes of tanning, the materials used, and the methods of their application.

Structure of the Skin. Although the skins of the various animals seem at first glance to have very little in common, they present, on closer examination, much similarity of structure. The differences in texture and thickness, on the other hand, make their practical application vary greatly. The skins of lizards, alligators, fish, and serpents differ from those of the higher animals in that the epidermis becomes harder and forms scales.

The skin is not merely a covering for the animal, it is at the same time the seat of the organs of sense and of certain important secretions. It consists of two principal layers, the *epidermis* (*epithelium*, *cuticle*) and the *corium* (*derma*, *cutis*, or true skin). The *epidermis* is very thin as compared with the true skin which it covers, and is entirely removed preparatory to tanning; it nevertheless possesses important functions. Its inner mucous layer, which rests upon the true skin, is soft and composed of living nucleated cells, which multiply by division and form cell-walls of *keratin*. These are elongated in the deeper layers, and gradually become flattened as they approach the surface, where they dry up, and form the horny layer that is being constantly worn away, thrown off as dead scales of skin, and renewed from below by the multiplication of the cells.

It is from the epithelial layer that the hair, as well as the sweat and fat glands, are developed. Each hair is surrounded by a sheath continuous with the epidermis, and in which the young hair usually grows as the old one falls out. Near the openings of the hair-sheath upon the surface of the skin the ducts of the sebaceous or fat glands pass into

the sheath and secrete a sort of oil to lubricate the hair. The base of the hair is a bulb, enclosing the hair papilla, which is a projecting knob of the true skin and which, by means of the blood-vessels contained in it, supplies nourishment to the hair. The hair bulb is composed of round soft cells, which multiply rapidly, and, pressing upward through the hair-sheath, become hardened, thus increasing the length of the hair.

The process of development of the sudoriferous or sweat glands is very similar to that of the hair. They consist of more or less convoluted tubes with walls formed of longitudinal fibers of connective tissue from the corium, lined with a single layer of large nucleated cells, which secrete the perspiration.

Besides the hair, and hair-sheaths, and the sebaceous and sudoriferous glands, the epidermis layer produces other structures of a horny character, including horns, claws, and nails, which, both chemically and anatomically, are analogous to exaggerated hairs. This is apparent in the quills of the porcupine. The whole of the epidermis, together with the hairs, is separated from the corium by an exceedingly fine membrane called the *hyaline* or glassy layer. This forms the very thin *grain* surface of tanned leather, which is of a structure different from the rest of the corium.

The structure of the corium or true skin is quite different from that of the epidermis. It is composed principally of interlacing bundles of fibers known as *connective tissue*, and cemented together by a substance more soluble than the fibers themselves. These fiber bundles are loosely interwoven in the middle portion of the skin, but become compact again near the flesh. The outermost layer, just beneath the epidermis, is also very close and compact. The skin is united to the animal by a network of connective tissue (*panniculus adiposus*), which is frequently full of fat cells and is then called *adipose tissue*. This portion, together with some actual flesh, is removed in the process of *fleshing*.

Ordinarily the corium or true skin is the only portion used for leather. To obtain it in a suitable condition for the various tanning processes, the hair or wool, together with the epithelium, must be completely removed without damaging the skin itself; and special care must be taken that the grain, or portion next the epidermis, does not suffer injury during the treatment.

Classification of Pelts. The pelts of animals come to the tanner in three conditions: *green* (fresh from the animal), *salted* (where salt has been rubbed on the flesh side), or *dried* (usually stretched on boards in the sun). The pelts so received are divided according to size into three general classes, namely: *hides*, *kips*, and *skins*. *Hides* comprise pelts from large and fully grown animals, such as the cow, horse, camel, and walrus. These form thick heavy leather, used for shoe soles, machinery belting, harness, and other purposes where stiffness and strength, combined with wearing qualities, are necessary. They are also cut into splits for use as shoe uppers, bag, case, strap, automobile, carriage, fur-

niture, and upholstering leathers. *Kips* are the skins of undersized animals of the above species. *Skins* are obtained from small animals, such as calves, sheep, and goats. Kips and skins yield a lighter leather than hides, which is suitable for a great variety of purposes, such as uppers for shoes, pocketbooks, book bindings, gloves, and fancy leather. Pelts vary in thickness and texture in different parts, being thicker on the neck and butt than on the flank and belly. The same species varies greatly according to the climatic conditions under which they are raised, and to their breeding and feed. They often show injuries like cuts, brand-marks, grub holes, and sores caused by the bot-fly or warble. Diseased hides are sometimes found and are a source of great danger to the tanner on account of the contagious nature of some of the diseases, especially anthrax.

Soaking. Whether the skins or hides are green, green-salted, or dried, they must first be soaked in water to remove the dirt and blood in the case of green stock, salt in the salted, and hardness in the case of the dried. It is very essential that the pelts should be free from all foreign matter before entering the limes or other unhairing solutions, as the presence of salt greatly retards the plumping, and the presence of albuminous matter is apt to set up an undesirable fermentation in the after treatments. When perfectly soft and well washed, the skins or hides are removed from the *soaks*, thrown over a rounded beam, tails and ear-laps trimmed, and any adhering portions of flesh removed.

The time of soaking varies from one or two days to several days, depending upon the thickness of the hide and the age and temperature of the soak. Putrid soaks, formerly used to quite an extent, soften much quicker than fresh ones, but great care is necessary in using them lest the decomposition attack the hide fiber itself. In the case of heavy hides that soften very slowly, it is advantageous to run them in a drum for a short time with water at a temperature of about 40° F., the tumbling movement materially aiding in the softening process. The addition of small amounts of alkali or acid to the soak water materially shortens the time of soaking and prevents the excessive loss of hide substance. For this purpose 0.1 per cent of caustic soda on the weight of the water is very satisfactory. Sodium sulphide, borax, and sodium carbonate may also be employed, in which case about 0.3 per cent should be taken. During the past few years formic acid has come into use, about 0.1 per cent of the weight of the water being required. When properly soaked, the stock should be free from hard spots and in a soft condition.

Water for Tannery Purposes. Water is used in the tannery for soaking and washing, making limes, preparing bates or puers, leaching barks, and dissolving extracts, also for steam boilers, and in dyeing. For all of these purposes the water shou'd be as pure as possible. The tannery must be located in a section where a good water supply is available, and the water, if hard, must be softened by chemical means. The most objectionable features of a bad water supply are its temporary and perma-

nent hardness. Both may be removed by a proper softening agent, such as sodium carbonate. The treatment should be carried out in tanks, and the sludge allowed to settle before use. A small amount of hardness is not harmful, however, and up to ten parts of solids per hundred thousand may be disregarded. Water possessing temporary hardness will cause the following objectionable conditions: When leaching, the calcium and magnesium carbonates in it combine with the tannin to form an insoluble substance with no tanning properties. In dissolving basic dyes with this kind of water there is a precipitation of the color base, which renders part of the dye useless. Further, as this precipitate is deposited on the skin, it causes uneven dyeing and gives rise to spots and streaks.

Permanent hardness is very objectionable in water for boiler purposes, but otherwise is not so harmful as temporary hardness. The presence of calcium and magnesium sulphates is usually the cause of permanent hardness, and these salts being already combined with a strong acid can have no action upon the tannic acid during the process of leaching. There might possibly be a slight tendency to lessen the solubility of the tannins, however, but this could be overcome by softening water of extreme hardness. One danger from water containing calcium and magnesium sulphates arises during the process of scouring and fat-liquoring, when one part of lime, reckoned as carbonate, destroys twelve parts of soap, producing a sticky and insoluble lime soap which adheres to the fiber and is very difficult to remove.

Mud under any circumstances is objectionable, for it usually contains organisms that encourage the putrefaction of hides during the soaking process. It also almost always holds iron, which either produces stains or gives a dark-colored leather. Sodium sulphate is probably inoperative. Sodium chloride, on the other hand, prevents plumping, and may be the cause of thin and soft leather, and in large amounts will greatly impede the proper exhaustion of many tanning materials.

Fleshing. After being soaked, the skins are usually *fleshed*. This operation removes any fat or flesh left on the pelt by the butcher, and consists in working the hide over a beam and using a sharp knife. In nearly all modern tanneries, however, the beam has been replaced by machines (Fig. 369) for the purpose.

The type of machine employed for fleshing skins differs somewhat from that used for hides, although the operation is similar in each case. The essential feature of the machine is a cylinder with spiral blades arranged right handed on one side, and left handed on the other. By means of this kind of blade the flesh is easily removed and the hide stretched in all directions.

Depilation. By the term depilation is meant the removing of the hair and epidermis. This is necessary in all kinds of leather, except that

used for furs. The soft mucous matter of the epidermis is affected, and the hair loosened without materially injuring the true skin.

Sweating. The oldest method of depilation seems to have been by incipient putrefaction, or "sweating," as it was called. The hides were allowed to remain in piles in a warm, damp room until the mucous matter connecting the epidermis with the dermis had decomposed. This loosened the hair without injuring the true skin. This method, however, often

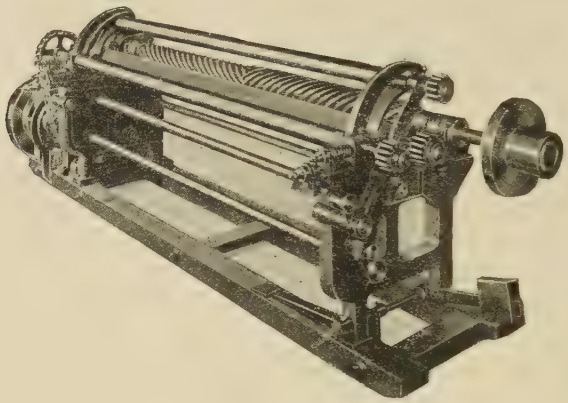

FIG. 369.—Fleshing Machine.

resulted in damaged stock, so the process was improved upon by allowing the hides to hang in a closed, damp room or cellar called a "sweat pit." Two general methods are employed known as "cold sweat" and "warm sweat."

Cold Sweat. The cold sweat method is very largely used in this country, especially for unhairing dry hides for the manufacture of sole leather. The sweat pit is a structure usually built above ground and protected from outside atmospheric influences by means of an outer and inner wall filled in between with tan bark or other material to prevent loss of heat by radiation. The temperature of these pits is controlled by means of steam pipes running under the false flooring and by a sprinkler system to provide moisture and decrease the temperature in case of necessity. The temperature is maintained at about 70° F. The hides are hung on hooks, each chamber holding a single pack. The sweating lasts usually four or five days. Near the end of the operation the stock is carefully examined, and in order to retard putrefaction, those hides showing the first signs of slipping are dropped to the floor where it is cooler than higher in the pit. At the conclusion of the process the hides are thrown into lime liquors for a short time to remove the slimy feel and to slightly plump the stock. The value of this process depends upon the fact that the hides are left in a firm condition without any appreciable loss of hide substance, but even when most carefully conducted, there is great danger from

excessive putrefaction with a consequent damage to the grain. Although this process has its disadvantages, dangers, and shortcomings, it is very widely used and no doubt will be continued for some time to come.

Warm Sweat. The warm sweat method is very similar to the cold sweat process, except that the temperature is higher, about 80° F., and the time of treatment somewhat shorter. It is applied more especially to sheepskins and is known as "staling." This process has not been adapted to any extent in this country.

Liming. Lime is the most common agent for unhairing, although it also has disadvantages. In preparing the lime solution a quantity of fresh lime (calcium oxide) is slaked by placing in a shallow tank, similar to that used by builders, and adding sufficient water to thoroughly moisten it. At the end of one or two hours it becomes heated and falls to a powder. Sufficient water is added to form a thick paste, which may be kept for seevral weeks or even months without much change. When required for use a suitable amount is dug out, stirred with water to remove rocks, and then run into the pits. As only the lime in solution is available for unhairing, the addition of a large excess is unnecessary. It is essential simply to provide a surplus of solid lime to replace that taken up by the hide. It is impossible to set any fast rule as to the proper quantity of lime, but a safe margin is 10 pounds for each 100 pounds of hide.

The usual method of liming is to place the hides one at a time in the lime solution, taking care that each hide is well immersed before entering the next one. The hides are taken out (*hauled*) each day, bettered, and the liquor well *plunged up*, in order to distribute the undissolved lime throughout the pit. They are then thrown back (*set*), care being taken to spread them out fully. In some yards the hides are joined by hooks (*toggled*) and reeled from one pit to another, or to the same pit. Sometimes hides are suspended in the liquor, and the limes are kept in motion by means of a paddle, or by blowing in air. The most common means, however, of agitating the liquor is by the ordinary paddle box run at intervals during the day.

The action of lime on the hide is to swell up and soften the epidermis cells, dissolve the mucous layer, and loosen the hair so that on scraping with a blunt knife, both the epidermis and hair are easily removed. The action on the true skin is very vigorous, causing the hide to become plump and swollen, and, at the same time dissolving the cementing material of the fibers, thus causing them to become split up into finer fibrils. This swelling is probably due to hydrolysis of the albuminous matter and to the formation of a lime soap. Not only does the liming process remove the hair and epidermis, but it also is of value in the reflesh-ing process, as it gives to the hide a greater firmness, very desirable when working with the knife or on the machine. The time of liming varies with the season of the year and with the kind of stock treated; it may run from three to thirty days. The age of the lime greatly influences the time

of treatment as well as the character of the finished product. Old limes unhair much quicker than fresh ones. It is often customary to place the hides in an old lime for several days, or until the hair and epidermis have started to loosen, then change them to a fresh lime, which produces the desired plumping of the fibers. Great care, however, must be taken that the limes do not become too old especially in hot weather, for this condition will be very apt to produce a transparent swelling of the tissue with destruction to the fiber. In modern practice old limes are very little used.

Arsenic Sulphide. When the *red sulphide of arsenic*, As_2S_2, is dissolved in hot water and added to lime it increases its depilating efficacy. It is especially good for fine leathers, to which it gives the necessary stretch, softness, and clearness of grain, without the loss of hide substance and the loosening effect caused by ordinary liming. The amount used varies somewhat, but may be said to run from 0.1 to 0.4 per cent of realgar and 4 to 6 per cent of lime, reckoned on the weight of the green skins.

Sodium Sulphide. This substance when employed in strong solution, 5 per cent or over, has the effect of rapidly reducing the hair and epidermis to a sort of pulp, which may be easily swept off with a broom or even washed off in the drum. The operation is usually conducted in a paddle and takes about two hours for the complete removal of the hair and epidermis. The action on the hide substance, and especially upon the cementing material, is very slight, although the grain is swollen and temporarily rendered somewhat tender. As this strong solution destroys the hair it is only used on such stock as goat skins, where the hair is of minor importance. On the other hand, when used in weak solutions, 0.25 per cent or less, in conjunction with lime, the hair is but little injured, the hair roots and dirt being rapidly loosened with a result somewhat similar to that produced by arsenic sulphide. Sodium sulphide in strong solution produces a false grain. This very undesirable condition may be overcome by using a dilute solution and running for a longer period, or by introducing 25 per cent of calcium chloride on the weight of the sulphide used.

Arazym. It has recently been discovered by Dr. Otto Röhm that hides and skins can be unhaired and bated in one operation by means of *tryptase* in an alkaline solution. If this proves successful from a practical standpoint it will tend to materially change the old-time beam-house methods. By this process the soaked and fleshed stock is placed in a 0.1 per cent solution of caustic soda for twenty-four hours to allow plumping and opening up of the fiber bundles. The caustic soda is then drawn off, the skins washed in running water for a short time, and enough sodium bicarbonate introduced to make a 0.1 per cent solution. The temperature of the water is raised to 90° F. and sufficient *arazym* added to give a 0.1 per cent solution. The stock is run in this solution from twenty-four to forty-eight hours or until unhaired.

Calcium Sulphydrate. This compound is a very powerful depilatory,

but is little used on account of its unstable character. It is probably formed to some extent when sodium sulphide and arsenic sulphide are added to lime. It may be produced by passing hydrogen sulphide into milk of lime until the latter becomes saturated. This is the substance largely sold as a patent depilatory for removing superfluous growths of hair.

Unhairing. When the process of depilation is complete the skins or hides are removed from the pits and allowed to drain for half an hour or more. They are then placed on the beam and the hair removed by means of a blunt knife. In recent years various machines have been devised to remove hair, and these have been brought to such perfection that the old method of hand work has been almost entirely eliminated. The unhairing machine (Fig. 370) is very similar to the fleshing machine, but is provided with a blunt knife which works against the grain of the stock.

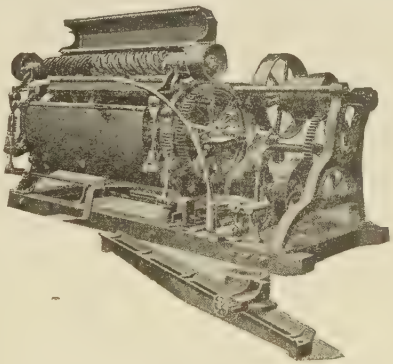

Fig. 370.—Unhairing Machine.

Bating. It is very essential that the lime, or other depilating agent, should be completely removed after it has done its work, for when brought into contact with tanning materials, it has a very harmful action. It also has a tendency to weaken the fiber and produce a harsh-feeling product. For most leather it is necessary not only that the lime be completely removed, but that the skin be brought from its swollen to a soft and open condition. To accomplish this with the heavier classes of dressing leather, such as split hides, kips, colt, and calfskins, the stock is run in a weak fermenting infusion of pigeon or hen manure. The time of immersion depends upon the strength of the liquor and the nature of the pelts under treatment.

Puering. This very similar process is applied to the finer and lighter skins, such as glove and glacé kids and moroccos. Dog manure is substituted for that of birds. As the mixture is used warm and the skins are thin, the process is complete in a few hours. Neither bating nor puering is very effective in removing lime, but seem to act upon the hide substance by means of bacterial products, causing the pelt to fall, that is, to become soft and flaccid. Great care must be exercised in this treatment, in order to prevent possible decomposition of the hide, or what is known as "running of the grain," where the action becomes local and the grain is eaten away in spots. During electrical storms the action, it is claimed, becomes intensified and may result in a complete decomposition of the pack, unless the skins are drawn out or the liquor greatly diluted.

When the skins are removed from the dung infusion, they are slightly alkaline in reaction from excess of lime and ammonia. This condition must be removed before the actual tanning process. The neutralization, accomplished in various ways, is known as *drenching* and *pickling*.

During the past few years several patented bates have replaced the older methods to a very large extent. These bates are of a chemical nature, a fermentative nature, or both. Of these preparations the ones now being used are the following:

Oropon. This material is composed of ammonium chloride, wood fiber, and dry pancreas. It is put on the market as a dry powder and has this advantage that no previous preparation is necessary. The quantity required is from $\frac{1}{2}$ to 1 per cent of the weight of the stock at a temperature of from 90 to 100° F. The first action, the neutralization of the lime by the ammonium chloride, causes the stock to fall at once; the enzymes than exert a solvent action upon the cementing material of the hide causing it to become open.

Puerine. This compound must be fermented before use. Once started, however, it can be run for several months, there being necessary only the addition of fresh material for that exhausted.

Chemical Bates. For certain classes of leather ammonium butyrate, lactic acid, or formic acid have been found to give very satisfactory results. All of these are very active deliming agents. Ammonium chloride has a solvent action upon the lime and is used in many of the patent bates. Boric acid is occasionally employed, because it has power not only to remove the depilating agent, but also to hasten the tannage, giving a good color and smooth grain. Where chemicals alone are employed the results differ from those obtained with bacterial bates.

Drenching. Drenching is sometimes used as a substitute for bating, but usually follows the bating process. It not only serves to remove the lime completely, but tends to slightly plump the skins. The drench liquor is prepared by allowing an infusion of bran in warm water to ferment under the action of special bacteria which develop lactic and acetic acids. When a bath is once prepared it can be used continuously by drawing off part of the liquor and adding fresh portions of bran and water. In neutralizing by this method the skins are entered and the liquor moved occasionally to get a uniform contact. As fermentation becomes well established during the night, the gas produced makes the skins rise to the top. The night watchman then forces them under again with a heavy pole. On rising a second time they are free from lime and in a soft, open condition. This open condition is very essential in soft leather but not desirable in harness, or other kinds of firm and heavy leather.

Pickling. This method usually consists in running the skins in a concentrated salt solution containing a small amount of sulphuric acid. The ratio between salt and acid is usually 8 pounds of salt to 1 pound of

acid. The solution should stand 1.060 sp.gr. (8° Bé., 12° Tw., 60° Bk.). In some tanneries the pickling is done in the paddle, and fresh acid introduced after each pack has been removed. If the pickle has the correct acid strength, 15 cc. of normal sodium hydroxide will neutralize 100 cc. of the liquor, using phenolphthalein as an indicator. The salt should be replenished by adding a sufficient amount to keep the specific gravity up to 1.060. The usual practice in this country is to pickle in the drum, which has the advantage of being more rapid and does not depend upon chemical control.

The Tanning Operation. The term *tanning* was originally applied to the treatment of hides and skins with some vegetable product containing tannic acid. With the introduction of chemical methods for preserving the hide substance the old term has been retained, so that the term *tanning* may mean a treatment not only with mineral salts, oils, or aldehydes, but also with vegetable substances containing tannic acid.

Vegetable Tannage. For the actual tanning operation the liquor used depends entirely upon the nature of the skins or hides and upon the kind of leather to be turned out. There are, however, three general methods. The first consists in suspending the stock in a solution of the tanning material; the second, carried out in a paddle, keeps the stock in constant motion during the whole or part of the operation; the third consists in tumbling the stock in a drum or pin mill during the whole or part of the operation. For heavy hides the time of treatment is, of course, very much longer than for light skins.

Harness Leather. The bated hides coming from the "*beam house*" are placed in an acid liquor to neutralize the lime. This is done in *stick pits* or *suspenders*, the name coming from the fact that the hides are suspended by the butts from sticks placed across the pit. The liquor in the first pit is very dilute and nearly exhausted, having a density of about 8° Bk. From day to day the liquor, consisting of a mixture of vegetable tanning materials, is changed, so that a gradual increase in its strength is obtained. After the hides have remained in the suspenders from fifteen to twenty days they are transferred to a series of pits called *layers*, containing a stronger liquor. The weakest liquor from the youngest handler pit is run daily to the suspenders, a new and stronger liquor being run into the pit holding the oldest and most tanned pack. As this pack is removed the next in age takes its place, while the youngest pack enters the pit containing the weakest liquor. In this manner each pack receives a change of liquor of graduated strength, passing from about 20° Bk. to one of 30° Bk. In the layers the hides are completely struck through or tanned, which usually takes from thirty to fifty days.

On removal from the layers the stock is thoroughly washed to free it from insoluble matter, set out, and then *scoured* to remove the "bloom." The scouring or cleaning process is accomplished by placing the hides on the movable table of the scouring machine, where they are violently

scrubbed with a coarse brush and stone slicker, while a stream of water is allowed to play over the surface.

In order to secure a better and more uniform color it is customary to *strip* or remove a part of the surface tannage by means of borax or weak alkali. This is usually carried out in the drum, and the excess of alkali neutralized with oxalic, sulphuric, lactic, or formic acids. The cleared hides are then cleaned by thorough washing and retanned with sumac or other light-colored tanning material. Previous to the retanning it is also customary in most shops to remove a small skiver from the flesh-side so that the hides will have a uniform thickness and appearance.

The object of this operation is to surround the fibers with fat and oil, which serves to lubricate them and render the leather more pliable, while at the same time it gives to the stock more body or weight. The most common process consists in placing the *sammied* (damp) hides in a drum, heated to about 140° F., and running in the melted stuffing material through the trunnion. Many kinds of stuffing greases are used. One which gives very satisfactory results consists of a mixture of tallow and cod oil. After running for about half an hour the hides are removed and set out while still warm. This setting out is accomplished on a machine of which there are several types. In the setting out the excess of grease is removed and the stock given a mild stretching. Stuffing may also be done by hand, in which case a dubbing of cod oil and tallow is applied to the flesh and the hides set on the grain on a table. The well-set leather is now rolled on the flesh, coated with cod oil, and hung up to dry. When thoroughly dry the leather is snuffed on the grain either by hand or on the machine. In the case of russet leather a colored finish is applied to the grain and the stock smooth plated. If black leather, the stock is usually colored with hematine and a striker. In either case a top finish of stearine is applied and the leather brushed for finish.

Strap Leather. For this class of leather the same process is used as for harness up to the point where the stock leaves the stick pits. At this stage the hides are usually split to gauge and the grain only placed in the layers. By this splitting operation the time in the layers becomes much shortened. From the layers the hides are washed and bleached and retanned with sumac, washed again, and set out on the machine. They are next hand stuffed with a dubbing of tallow and cod oil and tacked out on frames. When dry the leather is stripped, given a gum or oil finish on the flesh, and rolled. It is then hand or machine snuffed, and given a finish of dextrine applied to the grain. The stock is now smooth plated and coated with stearine. After standing twenty-four hours, the leather is brushed for final finish.

Sole Leather. The green-salted hides are shaken free from salt, trimmed, and cut into sides. The sides are thrown into water, where they are allowed to remain for twenty-four hours. They are then removed from the water, placed in the drum, and turned for one-half hour. If not

sufficiently soft they are again returned to the still soak for another day.

In liming this grade of stock the hides are first treated with a mixture of 10 per cent hydrated lime and 2 per cent sodium sulphide and left in the liquor one day. On the second day they are transferred to another paddle or pit containing 10 per cent of lime and 1 per cent of sodium sulphide. On the third day the hides are transferred to straight lime liquor containing 10 per cent on the weight of stock. On the fourth and fifth days they are also changed to straight lime. On the sixth day they are thrown into the warm pool for half an hour, after which they are ready for unhairing.

On removal from the warm pool, the sides are placed on a table, spotted for white hair, and then the remainder of the hair removed by the unhairing machine or over the beam.

The unhaired stock is next fleshed on the machine and thrown into a wash paddle for one-half hour. It is subsequently skudded on the beam, placed on sticks, and put into a cold 0.6 per cent solution of lactic acid overnight.

On removal from the cold pool, the sides are placed in the tail rocker liquor, which consists of an 8° Bk. solution of hemlock extract, chestnut extract, and myrabolans, or other combination, with an acidity of about 0.6 per cent. The liquor is changed from day to day until, by pressing forward, it increases in strength to about 12° Bk. This should take about fourteen days.

The stock coming from the head rocker is placed in the first layer liquor, where it is further tanned in a mixture of tanning extract, standing at about 20° Bk. The liquors are pressed forward for twenty days, the stock coming out of a 25° Bk.

The second layer is usually made up of straight chestnut extract at 30° Bk., and the stock remains in it for about seventeen days. As the sides are thrown into the pit, each one is sprinkled over with chestnut oak bark chips.

The third layer liquor is commonly made up of a 40° Bk. ordinary quebracho extract, and the stock is piled down in it for thirty days.

As the hides are removed from the last layer, they are thrown into a warm quebracho liquor for about one hour and then, after pressing, are transferred to the mill. A 100° Bk. ordinary quebracho extract at 130° F. is introduced and the stock extracted in it for one hour. From the extract mill the stock is thrown into a tempering pit containing clarified quebracho extract and allowed to remain for four or five days. From the tempering pit the hides are placed on sticks and dipped for five minutes in a warm solution of sodium carbonate, followed with a five-minutes' dip in warm water, than in a solution of sulphuric acid, again in a second solution of sulphuric acid, and finally in warm water. From the bleach the stock is again pressed and is ready for filling. To the stock

in the drum is added a strong solution of glucose syrup, magnesium sulphate, and sole leather oil, and the hides are run in this compound for one-half hour.

Sole leather should be dried out very slowly by placing it in a cold, dark loft. After two days the temperature may be raised if desired.

The dried sides, on removal from the loft, are dipped in a warm dilute solution of glucose and magnesium sulphate and piled down overnight. The wet stock is given a liberal coat of sole leather sponging compound and is then rolled while wet. This should be done in the morning, so that the stock may again be rolled in the afternoon when dry. Many tanners do nothing more after rolling, but some prefer to apply a coat of brushing compound, and, when this is dry, pass the stock through the brushing machine.

Belt Leather. For belting leather the same process is followed through the liming and tanning up to the extract mill. This class of leather, however, is not filled. The stock coming from the yard is cut into belting butts, washed, bleached, retanned with sumac, and scoured. It is then stuffed in the hot mill with a mixture of tallow and cod oil, and, after being chilled, is set out by hand or on the machine.

From the setting-out machine the hides are placed on frames, where they are given as much of a stretch as possible and allowed to dry in a state of tension. On removal from the frames the hides are given a coat of wax, shellac, gelatine, blood albumen, or other finishing substance and, after rolling on the *jack*, are ready for the market.

In the tanning of heavy leather the above treatment is sometimes varied by cutting the hides into *bends* and *bellies;* or into *butts* and *shoulders*. The subsequent treatment is somewhat modified for the different portions. The tanning materials used for heavy leather vary, consisting either of one or several tanning products. The density of the liquor employed may also vary within rather wide limits.

Vegetable-tanned Calfskins. In preparing calfskins for the tanning process they should be well beamed and bated until they are soft and open. The washed skins are then suspended on sticks and allowed to hang in the tan liquor as described under hides. The strength of the liquor, however, may be somewhat changed, although 8° Bk. is very satisfactory at the start. The strength is increased uniformly for six days when the stock should be completely struck through or tanned. The skins are then removed from the suspenders, washed, and horsed up to drain. When in the proper sammied condition they are shaved and retanned in sumac, to which a small amount of sulphuric acid, oxalic acid, formic acid, or formaldehyde is added. The retanning may be carried out in a drum, but the paddle is preferable. When the retanning is complete the skins are again washed, treated with about 3 per cent of soluble oil, set out, and hung up to dry.

Vegetable-tanned Sheepskins. Sheepskins come to the tanner in

the pickled condition, containing sulphuric acid and salt. They are usually washed free from the pickle with a strong salt solution before they enter the tan liquor. These skins may be tanned in pits as described for calfskins, except that it is necessary to have a certain amount of salt in the solution. The tanning may also be carried out in the paddle.

A very rapid method for tanning sheepskins and *skivers* (split sheepskins) consists in running the stock, without removing the pickle, in a drum with 25 per cent of solid quebracho extract, or its equivalent of other tanning material, and 10 per cent of salt. The time necessary is about one and one-half hours. When the skins are tanned they are thoroughly washed and hung up to dry. As sheepskins contain a large amount of fat they should be degreased before the coloring and finishing operations. This is accomplished by dipping in naphtha. If it is not convenient to use the naphtha treatment, they may be run in a drum with $\frac{1}{2}$ per cent of soda ash, washed, the alkali neutralized with sulphuric or formic acid, and the skins again washed. When dry the skins are buffed on the emery wheel, retanned, and colored.

Vegetable-tanned Goatskins. At the present time practically all goatskins are tanned by the two-bath chrome process. For certain kinds of fancy morocco leather, however, sumac or other vegetable tanning materials are employed. The bating of goatskins is more difficult than that of other pelts, and a more active substance has to be employed.

Chrome Tannage. The action of chromium salts upon hide substance was first studied by Knapp in 1858, but his investigations led him to conclude that their application was of no practical value. Although other investigators took up the matter, it was not until 1884 that any really important advance was made. At this time Augustus Schiltz patented his "two-bath process," while the skins or hides are treated with a solution of chromic acid, produced by the action of hydrochloric acid upon sodium or potassium dichromate, and afterward with a solution of sodium thiosulphate and hydrochloric acid. The hide substance takes up the chromic acid, which is subsequently converted to the basic condition by means of the "hypo." In 1893 Martin Dennis made a study of the action of chromium salts as previously investigated by Knapp, and perfected a method for "one-bath tannage," on which he was granted numerous patents.

Two-bath Chrome Process. While the details involved in the application of this process vary, nevertheless chrome tanning is uniformly carried out either in a paddle or drum. Different kinds of leather require different percentages of the chemicals. In the drum tannage 6 per cent sodium or potassium dichromate and 3 per cent of hydrochloric acid, regulated on the weight of the wet skins, are dissolved in sufficient water for the proper handling of the stock. The skins or hides are placed in the drum and the chrome solution added, the drum being kept in motion. The hides or skins are worked in the solution until they have taken on a uniform yellow

color completely struck through. They are now removed from the drum and freed from the superfluous liquor either by horsing up overnight or by putting out; the latter operation may be done by hand or on the machine. After standing for twenty-four hours the chromed stock is returned to the drum and run for about one and one-half hours with a solution of 12 per cent of sodium thiosulphate and 6 per cent of hydrochloric acid. On removal from the drum the stock should have a blue-green color and be uniform throughout. If thoroughly tanned, no curling will take place when a strip is placed in boiling water. The stock is horsed up for twenty-four hours to allow the chrome to set, is neutralized by running for half an hour in a $\frac{1}{2}$ per cent sodium bicarbonate solution, washed in running water for half an hour, horsed up, and allowed to drain.

The reactions taking place in this process are represented in the following equation:

$$Na_2Cr_2O_7+2HCl=2NaCl+2CrO_3+H_2O.$$

The CrO_3 produced forms a compound with the gelatine. The sodium thiosulphate now acts as a reducing agent upon the chromic oxide, converting it from the acid to the basic condition, the reaction taking place in two stages:

1. $2CrO_3+6HCl+3Na_2S_2O_3=3Na_2SO_4+3S+Cr_2Cl_6+3H_2O.$
2. $Cr_2Cl_6+Na_2S_2O_3+H_2O=Cr_2(OH)_2Cl_4+SO_2+S+2NaCl.$

The basic chloride of chromium held by the fiber is probably converted to $Cr_2(OH)_6$ by the action of the sodium bicarbonate used in washing.

One-bath Chrome Process. In this process the skins or hides, after coming from the puer, are washed with running water and run in a pickle for about one hour. The pickle is made by dissolving 8 pounds of salt and 2 pounds of sulphate of aluminium in a small amount of water, adding 1 pound of sulphuric acid, and making up to a density of 40 Bk. The object of this treatment is to neutralize any remaining alkalinity of the puer or lime, and to ensure the stock's being in an acid condition before it enters the tan.

Many methods for preparing a one-bath chrome liquor are in vogue. A very good liquor may be made by dissolving 10 pounds of sodium dichromate in 10 gallons of water, adding 6 pounds of syrup glucose (40 Bé.), and then very *slowly* introducing 10 pounds of concentrated sulphuric acid. A wooden vessel may be used for making up this liquor. A less violent action, however, is produced by adding the glucose last, but in this case stoneware or other acid-resisting vessels must be employed. A liquor, when prepared as above and diluted to 45 Bé., will give a product of such strength that 15 pounds will be required for each 100 pounds of pickled skins treated.

In using this method the necessary amount of reduced liquor (15 per cent of above liquor, equivalent to 4 per cent of dichrome) is dissolved

in a sufficient quantity of water for proper handling of the stock, and 5 per cent of sodium sulphate added to the solution. The pickled skins are placed in the drum, the door closed, and one-third of the solution introduced while the drum is in motion. At the end of fifteen minutes another third is added, and in thirty minutes the remainder. One-half hour after the last portion has been put in, $\frac{1}{2}$ per cent of sodium bicarbonate in solution is introduced, and the stock run for fifteen minutes longer. The hides or skins are then removed from the drum, horsed up overnight, neutralized with $\frac{1}{2}$ per cent of sodium bicarbonate, thoroughly washed, horsed up again, and allowed to drain.

Chrome tannage by either of the processes given above may also be carried out in the paddle, but in this case the time of treatment is somewhat longer. The advantage of the paddle tannage is that a smoother grain is obtained with less danger of " pipey " leather.

Alum Tannage. This process is employed especially for white kid, glove, and light-colored leather. There are many ways of applying the alum, and the following description simply serves to illustrate the method. The skins are lined, bated, and pickled in the usual manner. The solution necessary for 100 pounds is made by dissolving 10 pounds of sulphate of aluminium and 3 pounds of salt in 10 gallons of water; a solution of $1\frac{1}{2}$ pounds of soda ash is then dissolved in 2 gallons of water and added to the aluminium sulphate very slowly, with constant stirring; 30 pounds of flour is now triturated with some of the solution, added to the original solution, and finally 8 pounds of egg yolk introduced. The skins are drummed in this mixture for one hour and hung up to dry. After laying in the *crust* (dry condition) for several weeks, they are softened and again drummed with the above mixture.

Oil Tannage. The oldest tanning method of which we have any record was that in which the oil, fat, and brains of animals were used to preserve the pelts in a soft and non-putrescible condition. The present method consists in kneading the goods in contact with certain oils and soft fats. As the fibers slowly dry, the fats are worked in between them by means of the mechanical treatment which the goods undergo in the *stocks*. Each fiber is, therefore, separated from its neighbor in a non-adherent condition and at the same time is surrounded by a waterproofing material. Not only are the fibers surrounded by the oil, a vigorous oxidation also occurs, resulting in the formation of aldehydes and other insoluble oxidation products. The aldehydes, by virtue of their chemical activity, unite with the hide fiber, while the insoluble products coat the fibers mechanically. Oil tannage is used in the manufacture of chamois, buff, and buck leathers.

The flesh splits from sheepskins are used in the manufacture of chamois leather. The skins are given a thorough liming (from twelve to fifteen days), drenched, and the superfluous liquor removed by subjecting to hydraulic pressure. They are now drummed for half an hour to equalize

the moisture, then transferred to the stocks, one at a time, where cod oil is sprinkled over each skin. In the stocks the goods are worked for four hours, removed to the drying loft, and dried without heat until they assume an opaque condition. They are now resprinkled and restocked for another four hours, this time being dried to a brown color at 100° F. The stocking and drying are repeated several times with an increase in the temperature of the *heater* up to about 160° F. On coming from the final drying the skins are packed in a box, covered with matting, and spontaneous heating allowed to continue.

When the oxidation of the leather is complete it is dipped in water at 110° F. for a short time and then subjected to hydraulic pressure. The heavy grease, expressed by this treatment, is collected and sold for leather dressing under the name of *degras*. The skins are washed with a warm sodium carbonate solution, and the wash water neutralized with sulphuric acid, giving what is known as *sod oil*. The skins are next washed with hot water, nourished with cod oil and soft soap for one hour, squeeze rolled, and allowed to dry.

Aldehyde Tannage. The use of formaldehyde as a tanning material has recently been brought to the attention of the tanner by the patents of Payne and Pullman, but as yet has not become extensive. The leather obtained by this process resembles buff leather. It is very white, however, and needs no bleaching. The future of this method remains to be seen.

Finishing of Dressing Leather. After the leather is tanned by any of the methods given above it must be finished in such a manner as to meet the requirements of the various purposes for which it is to be used. Only a few of the most important operations in the finishing of leather will be given.

Vegetable Tanned Stock. On removal from the drying room the skins are dipped in water at a temperature of 110° F. and placed in piles, or horsed up for some hours until evenly wet through or sammied. The goods may also be sammied by dipping in warm water and then covering with damp sawdust.

To bring the leather to uniform thickness, it is shaved while damp either by hand or by the shaving machine. The type of machine is shown in Fig. 371. It is fitted with a spiral knife-blade of steel, half of which is right-handed and half left-handed. The leather is placed over a roller that may be pressed against the cutting end by pressing on a foot treadle. The knife-blades revolve at a very high rate of speed and are constantly sharpened by means of an emery wheel.

The operation of splitting has replaced shaving to quite an extent, especially for side leather, which is now almost uniformly split out of the limes. In this process the leather is sliced parallel to the grain surface, so that the split portions have the same area as the original leather. Among the numerous types of splitting machines the "band-knife"

type is the most popular. The machine (Fig. 372) consists of an endless double-beveled knife which passes around two pulley wheels, one of which is attached to power. The sammied leather is pushed toward the knife,

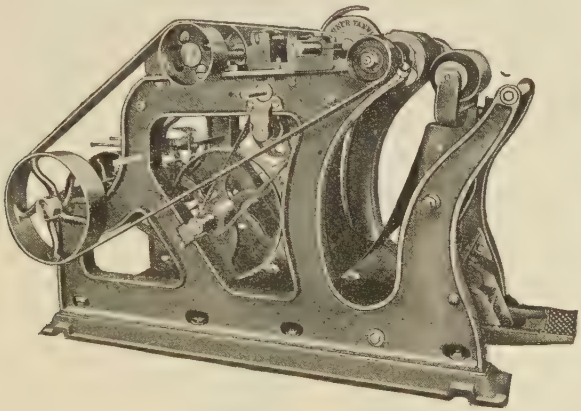

Fig. 371.

grain upward, by two feed rollers, the grain split passing over the knife and the flesh split under it. The thickness of the split can be varied from $\frac{1}{16}$ inch up to the thickness of the hide. In some cases, therefore it is possible to obtain as many as five good splits from one hide.

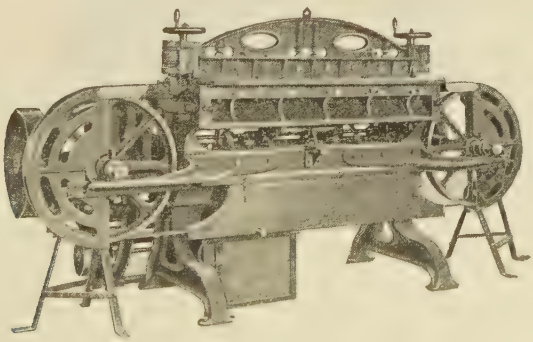

Fig. 372.

Colors on Vegetable-tanned Leather. The well scoured and cleaned goods are run for about fifteen minutes in a solution of $\frac{1}{2}$ ounce formic acid to each gallon of water. The excess of acid being removed, $\frac{1}{2}$ per cent of tartar emetic in solution is introduced, and the drum run for fifteen minutes. The excess of tartar emetic is removed. From $\frac{1}{2}$ to 2 per cent of basic color is now added (also a small amount of formic acid, should the water be hard) and the stock run for fifteen minutes. The plugs are next

drawn and the skins or hides given a thorough washing. To render the stock pliable, it is fat-liquored with either soap and oil or with soluble oil, horsed up for several hours, set out, and tacked up to dry.

Black on Vegetable-tanned Leather. To produce this color an ammoniacal solution of hematin is prepared, brushed evenly over the surface, and followed by a striker of black iron and copper sulphate. Nigrosine and other coal-tar blacks are also used for the same purpose.

The skins or hides coming from the boards are in a very hard condition and must be softened before they can be finished. This is done on the staking machine. This machine works the leather up by a sort of a kneading motion and at the same time exerts upon it more or less of a

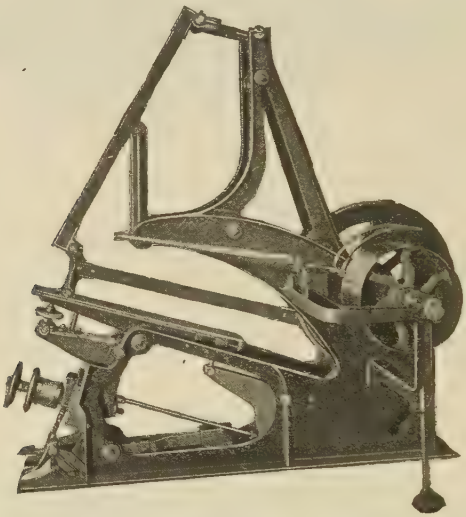

Fig. 373.

stretching action. After staking, the goods are spread on the table and coated with a mixture of flaxseed mucilage and milk, hung up to dry, and again staked.

The skins or hides after restaking and seasoning are rolled on the *rolling jack*. On this machine a steel roller passes over a bed in such a manner that a very great pressure is secured, the object being to work out the wrinkles and give a better appearance to the finished product. The stock after rolling is sometimes given a thin coat of oil and is ready for the market.

To give leather a high finish it is coated with egg albumen, blood albumen, or shellac, and then finished on the *glazing jack*. This machine is similar to the rolling jack, except that a glass cylinder is used in place of the steel roller, the glass sliding over the surface of the leather instead of rolling (Fig. 373).

Colors on Chrome-tanned Leather. The shaved stock is retanned in gambia or sumac, scoured, and then dyed as under the method for vegetable tannage. Recently, however, other methods have come into use, whereby the process of retanning is eliminated. It has been found that some of the alizarine colors give very satisfactory results when applied in the proper manner. Direct colors are also being used with some success, and especially a combination of acid colors with the basic colors. The finishing of this leather is then carried out as under vegetable-tanned stock.

Black on Chrome Leather. The stock, after being shaved, is placed in the drum and enough water at 140° F. added to float it. While the drum is in motion 1 per cent of hematin crystals, dissolved in water at 140° F. made alkaline with ammonia, is introduced through the trunnion and run for fifteen minutes. Without removing the hematin a solution of $1\frac{1}{2}$ per cent of chrome leather black is also added through the trunnion and turned for fifteen minutes longer. A sulphonate oil fat liquor is finally introduced and the stock milled for another half hour. The skins may then be set out, oiled off, and hung up to dry. On drying they are sammied in damp sawdust, staked, tacked, and finished as desired.

Patent Leather. This kind of leather is made by varnishing ordinary leather. The usual method is to first degrease the tanned stock. It is then given a daub coat of boiled linseed oil and lampblack, thinned to the proper consistency with naphtha. The excess of the coating is removed with the slicker and a mixture of linseed oil and pyroxlene applied. The hides are then baked and sunned, and rubbed down with pumice stone. They are given another coat of the linseed oil varnish with or without pyroxylene, baked, sunned, and rubbed. Coloring matter is usually added to the varnish, and sometimes several coats are applied.

Vegetable Tanning Materials. In those days when our tanners had the virgin forest to depend upon, hemlock and oak bark were the only vegetable tanning materials in use in this country, and they yet remain the source of greatest supply for tannin.

Hemlock Bark. The yearly cut of hemlock bark is between 800,000 and 900,000 tons, and of oak bark from 300,000 to 400,000 tons. The yield of hemlock has decreased about one-third in the last ten years, whereas the yield of oak bark has remained nearly stationary.

Because of increased production of leather during this period and because of the decrease in the peel of hemlock bark, it has become necessary to seek other sources of tannin.

Chestnut Extract. The first development to meet these conditions was the making of chestnut-wood extract, which has now reached a very important stage, from 450,000 to 500,000 barrels being produced yearly. In addition, chestnut wood is being used at many Southern tanneries directly in the leaches. Tanners have found the liquors obtained by

this method insufficient in strength for their purposes, so some of them have added to their leach houses evaporating plants that concentrate their liquors to a sufficient strength for their use.

A barrel of chestnut extract is practically equal to a ton or a cord of either oak or hemlock bark, and although the yield from various extract factories differs, generally a cord of wood (128 cubic feet) yields a barrel of 25 per cent tannin chestnut extract.

Quebracho Extract. Quebracho extract is made from quebracho wood, a product of the Rio de la Plata Valley in South America. This wood contains from 18 to 24 per cent tannin. The solid quebracho extract contains about 65 per cent tannin and is sold on this basis. The yield of extract is generally 1 ton of solid extract from about $3\frac{1}{2}$ tons of the wood. One ton of the solid extract is considered equivalent to 9 tons of oak or hemlock bark. There is now being imported about 60,000 tons of this solid extract or its equivalent in wood. As there are two factories manufacturing liquid quebracho in this country, the equivalency of this quantity of quebracho is 540,000 tons of oak or hemlock bark.

The tariff on this product was formerly $\frac{1}{2}$ cent per pound, but it has been raised to $\frac{3}{4}$ cent per pound in the present tariff bill.

Mangrove Bark. Mangrove bark and mangrove extract are also imported in quantity. Mangrove grows on the low shores of salt waters everywhere in the tropics. Along the Gulf of Mexico, mangrove averages, when properly cured, about 30 per cent tannin; that from the East Coast of Africa about 40 per cent tannin. East Indian and Borneo mangrove bark contains 30 to 40 per cent. This product enters free of duty, so that no accurate data are obtainable as to the quantity imported, but this, no doubt, is more than 20,000 tons annually, equivalent to more than 60,000 tons of oak or hemlock bark.

In the East Indies are two factories making solid extract from this bark, which comes upon our market as mangrove cutch; the quantity being brought in is not large now, on account of the duty of $\frac{7}{8}$ cent per pound, which the present tariff has placed on this product. If formerly came in free.

Myrabolans. Myrabolans are the fruit of an Indian tree, the harvest ranging from 30,000 to 45,000 tons per year. The United States is taking from one-third to one-half the production. Myrabolans contain about 30 per cent tannin. What is now being used in the tanning trade in this country will represent at least 45,000 tons of oak or hemlock bark. It is in the duty-free list.

Valonia. Valonia, the cup of an acorn, obtained in Asia Minor and Greece, is being imported in quantity. It contains about 40 per cent tannin. The harvest is from 50,000 to 60,000 tons per year. What is being brought into this country is equivalent to about 40,000 tons of bark annually. It is not subject to duty.

Divi-Divi. Divi-divi and wattle bark are other tanning materials, but they do not come into this country in any quantity.

Palmetto Extract. Palmetto extract and canaigre are not produced in sufficient quantities to be commercially considered. Sumac and gambier are imported in large quantities, but do not reach the same trade that uses our native barks and cannot be compared with them.

From the estimates given of what the various tanning materials in use here are equivalent to in bark, it is seen that in total 2,300,000 tons are represented, about one-third being imported materials. At a fair valuation, these materials cost the tanner about $23,000,000, the importations being about $7,000,000 per year.

Chemistry of Tannin. From a chemical point of view, tannins are divided into pyrogallol tannins, such as from chestnut wood, myrabolans and valonia; and catechol tannins, such as from quebracho, hemlock, mangrove, and oak bark. But from the tanner's viewpoint, the color and characteristics of the leather made from these various materials is of more importance.

Arranging these materials as to their color, that is, from a light yellow to a dark red, we have sumac, myrabolans, valonia, bleached quebracho, oak bark, natural quebracho, chestnut, West Indian mangrove, hemlock, and East African mangrove.

A tanner using oak can duplicate the oak color by matching with a combination of chestnut and quebracho. There are many combinations that can be arranged from these materials to duplicate the oak, hemlock, or union colors so long established as standards in the sole-leather trade.

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CHAPTER XLVIII

GLUE AND GELATINE

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Glue. Glue is an organic substance of varying chemical constitution obtained upon drying the solution yielded by boiling with water properly prepared animal matter such as skins, bones, etc. Stout soups which gelatinize when cold represent very impure glue solutions. In commerce glue appears in a great variety of forms, in rectangular sheets or cakes (sheet or cake glues), in wide or narrow strips (ribbon and noodle glues), in broken flakes (flake or chip glues), and ground or granulated in all degrees of fineness (ground and powdered glues); it is sometimes colorless and transparent, sometimes opaque, and it occurs in all shades of white, yellow and brown.

Gelatine. Gelatine is made from certain kinds of bones and parts of the skin, selected, washed and treated with especial care so that the resulting product is much cleaner and purer than glue. Being extracted at a lower temperature or with relatively little exposure to heat, less of the fluid disintegration products of the stock are formed, and the jellying power is therefore greater. Broadly speaking then, glue is impure gelatine. In fact some very light colored high test glues so closely resemble gelatine, that an investigation of the conditions of manufacture or the presence of certain chemicals, is the only practical way to differentiate between them.

The derivations of the terms glue (from the unused Latin verb *gluere*, to draw together) and gelatine (from the Latin *gelare*, to congeal, a word allied to the English chill, gelid, jelly), at once call to mind the principal properties of these substances, for glue is chiefly used as an adhesive, whereas gelatine is valued mainly according to its stiffening or jellying properties. Both are typical colloids, Graham having in fact formed this term from the Greek κόλλα = glue; and they consequently exhibit the characteristic properties of this interesting class of substances, which, in marked contrast to crystalloids, do not crystallize, do not readily diffuse, and are impermeable to each other.

Colloidal Condition. Instead of referring to colloids as a "class of substances," it would perhaps be more correct to speak, as Graham does (Phil. Trans., 1861, p. 183), of the "colloidal condition of matter," for most substances may exist in either the colloidal or the crystalloidal state, depending upon the nature of the solvent (e.g., certain soaps) or upon the conditions governing their formation (e.g., gold, silicic acid). The ultimate particles of colloids are much smaller than what we would ordinarily term a physical subdivision, but rather larger than chemical molecules; consequently their reactions stand midway between the physical and the chemical changes of matter, as may be seen by considering the properties of glue.

Glue absorbs a considerable quantity of cold water and swells up, yielding a jelly which, upon the application of heat, melts to a viscous sticky solution that gelatinizes again upon cooling. When dried at medium temperatures, glue can be again redissolved and redried indefinitely; and it is therefore called a *reversible* colloid to distinguish it from other colloids which, when once dried, are insoluble (i.e., silicic acid). When superdried at about 130° C., however, both glue and gelatine become insoluble, their constituent particles having approached too close to be again separated by simple soaking.[1]

Glue solutions will not diffuse through colloidal membranes (i.e., parchment paper and bladder), and their jellies are impermeable to other colloids. The solutions are coagulated by alum, formaldehyde and tannin, and also by chromium salts upon exposure to light. But these precipitates cannot be considered in a strict sense as chemical compounds, because their composition varies greatly with the conditions of their formation. They are nevertheless of great technical importance, forming the basis of the tanning process, for the glue yielding substances are rendered insoluble in like manner.

Chemical Constitution. We know comparatively little of the chemical constitution of gelatine and still less of the more impure and further hydrolyzed glue. The essential constituents of gelatine are carbon, hydrogen, oxygen, and nitrogen (other elements such as sulphur, phosphorus, etc., being present in absorbed impurities) and its empirical formula according to Schutzenberger and Bourgeois is $C_{76}H_{124}N_{24}O_{29}$; but such a formula does not give any information of value. On the other hand a study of the cleavage products of gelatine gives some insight into its extreme complexity. Skraup and von Biehler (*Monatshefte für Chemie*, 1909, Vol. XXX, p. 476), find that upon hydrolysis with hydrochloric acid, gelatine yields the following substances all of which, from the previous work of Fischer, Levene and others, have been shown to be contained in it.

[1] F. Hofmeister considers this as a regeneration of collagen, which he regards as the anhydrid of gelatine (*Chem. Centralbl.*, 1879, p. 74).

The " precipitated bone phosphate " as it is called, is largely used in the manufacture of " bone china "; and the " acid phosphate " is used in baking powders. In order to avoid an excess of lime, which would reproduce tricalcium phosphate, a filtered sample of the liquor is from time to time tested with molybdic acid solution, and the addition of lime stopped as soon as the failure of the ammonium phosphomolybdate precipitate to form, indicates that no more free phosphoric acid or acid phosphate is in solution. If an excess of lime be accidentally added, the error can be retrieved by the addition of a suitable quantity of the acid liquor. The precipitate is pumped or forced by compressed air into a filter press and washed free from calcium chloride.

The soft collagen after washing out the residual acid (using lime water to neutralize if necessary) may be made directly into glue, but it usually is dried at a low temperature, yielding commercial ossein.

Dentelles. The ossein made from button makers' refuse is commercially known as " dentelles "; it is frequently called " spectacles " because of the fancied resemblance to eye glasses, of pieces from which the round buttons have been cut.

Prepared Horn Pith. This is an ossein stock made from the cornillons or interior supporting bony core of the horns. As it is the only part of the osseous structure that does not come in contact with flesh, horn pith yields a singularly pure and high-class gelatine, and its porous structure renders easy its treatment and subsequent extraction.

Fish Stock. The heads, bones and skins of fish yield liquid glues which are not considered here. The swim-bladders of certain species of fish constitute what is known as isinglass.

Manufacture. The manufacturing operations at the glue factory are:

1. Preparing the stock;
2. Boiling the stock;
3. Treating and (4) drying the resulting glue solution.

Preparation. While the last two of these classes of operations are substantially the same for all stock, there are several methods of preparation, as might be expected from the great variety of raw materials.

Washing and Liming. Hide, sinew and ossein stocks after a brief preliminary soaking or washing in pure water to soften them and remove dirt, salt, etc., are placed in successive baths of lime water of gradually increasing strength, in which the stock swells up and becomes soft or " plump " so that it readily dissolves in the boiling kettle. The time required for liming varies with the stock and the season, always proceeding more rapidly in warm weather.[1] Thick dry hide pieces may take as long

[1] Hide pieces are often shredded or cut small to expedite the liming process, and the limes are sometimes " sharpened " with soda.

worn-out Turkish rawhide moccasins, and many other kinds of rawhide and parchment waste. Tanned skin yields no glue, although patents have been taken out for extracting the tanning materials and making glue from the skin thus made soluble.

"Dry stock" may have been either uncured or salted or limed before drying; "green" or wet stock may be "green salted" or "green limed."

Sinews. These come into the market fresh or green salted from the slaughter houses; they are also imported in dried state from South America, in which case they are frequently mixed with dried bulls' pizzles.

Bone. Quite a number of kinds of commercial glue stocks are produced from osseous tissue. The chief of these are enumerated below.

Green or Packer Bone. This consists of fresh sweet bone containing the marrow or bone fat and frequently adhering tendons. Such stock usually undergoes an immediate preliminary steaming at its place of production, by which the fat is separated and the keeping qualities of the bone so improved that it will stand transportation and storage. At the packing houses large quantities of fresh bone are produced in the canning departments. The long shin bones are sold to manufacturers of buttons, knife handles, etc. (whose refuse is later used), while heads, ribs, feet, etc., go direct to the glue factory. The hoofs and horns are usually first removed, for contrary to popular notion, they yield no glue at all. From cattle feet neatsfoot oil is rendered at a low temperature.

Country bone, which is chiefly butchers' offal and *junk bone* consisting of old dry bone from any source, are used mostly for the production of low grade glues.

Ossein. This is also called acidulated bone. It is prepared by leaching crushed bone in dilute (about 8 per cent) HCl, whereby the mineral constituents are dissolved, leaving a soft cartilaginous substance (collagen) which preserves the original shape of the fragment of bone. Before this process the bones are usually degreased in a closed steel tank with a volatile solvent (benzine or carbon tetrachloride) which is afterward distilled off from the grease and recovered. In the acidulation the main reactions are:

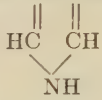
$$Ca_3(PO_4)_2+4HCl=2CaCl_2+CaH_4(PO_4)_2 \text{ (acid phosphate)},$$
$$Ca_3(PO_4)_2+6HCl=3CaCl_2+2H_3PO_4,$$
$$Ca_3(PO_4)_2+4H_3PO_4=3CaH_4(PO_4)_2.$$

From the acid solution the phosphoric acid is precipitated by the careful addition of milk of lime:

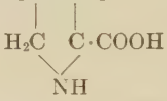
$$CaH_4(PO_4)_2+CaO=Ca_2H_2(PO_4)_2+H_2O,$$
$$2H_3(PO_4)_2+2CaO=Ca_2H_2(PO_4)_2+H_2O.^1$$

[1] In both the solution and precipitation of the bone phosphate other secondary reactions go on at the same time.

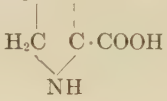
Glycine .....α-amino-acetic acid..... $CH_2(NH_2)\cdot COOH$
Lysine.....α-ε-diamino-caproic acid..... $CH_2\cdot NH_2(CH_2)_3CH(NH_2)\cdot COOH$
Alanine.....α-amino-propionic acid..... $CH_3\cdot CH(NH_2)\cdot COOH$
Phenylalanine..β-phenyl-α-amino-propionic acid... $C_6H_5\cdot CH_2\cdot CH(NH_2)\cdot COOH$
Leucine.....α-aminono-iso-caproic acid..... $CH_3(CH_2)_2CH(NH_2)\cdot COOH$
Aspartic acid...amino-succinic acid..... $COOH\cdot CH_2\cdot CH(NH_2)\cdot COOH$
Glutamic acid..α-amino-glutaric acid..... $COOH\cdot CH_2\cdot CH_2CH(NH_2)\cdot COOH$
Histidine..... β-imino-azole-α-amino-propionic acid $N{-}C\cdot CH_2\cdot CH(NH_2)\cdot COOH$



Arginine.....α-amino-δ-guanino-*n*-valeric acid...
$NH:C(NH_2)\cdot NH(CH_2)_3\cdot CH(NH_2)\cdot COOH$
Proline.....α-pyrrolidine-carboxylic acid..... $H_2C{-}CH_2$



Oxyproline....β-oxy-α-pyrrolidine-carboxylic acid.. $H_2C{-}CH\cdot OH$



Some of these substances may result from the decomposition of more complex constituents; in any event it is not yet known just how they are combined.

Raw Materials. Commercial glue stock may be divided into four classes:

1. Skin or hide.
2. Bone.
3. Sinew.
4. Fish stock.

Hide Stock. Most hide stock is produced by tanners, and as leather is more valuable than glue, only waste pieces of hide reach the glue-maker. The principal kinds of such stock are: "pieces," or heavy trimmings from dried, salted or limed skins (yield 18 to 50 per cent of glue); "fleshings," representing the scrapings from the flesh side (yield 3 to 40 per cent of glue); "skivings," which are parings from the hair or grain side of the skin or hide. Very frequently the yield of grease from fleshings exceeds both in percentage and value that of the glue especially in the case of "machine fleshings," which are usually thinner than those taken off by hand.

Calf, cattle, goat, sheep, deer, pig and horse skins are valued about in the order given.

A great variety of other kinds of hide waste also finds its way into the glue pot, as for example: *rabbit skin or coney stock*, a refuse produced by hatters who pluck off the fur for the manufacture of felt hats; *loom pickers*, representing discarded fragments of rawhide from textile machinery;

as six months to lime, whereas fleshings or thin skivings from hides limed at the tannery are frequently all ready to boil; coney stock, being very finely shredded, is usually boiled without liming. Practical experience is needed in this process, for an underlimed stock requires more time and heat to dissolve (thus injuriously affecting the quality of the glue), while overlimed stock is largely wasted in the washing process, which we will next consider.

The limed stock is taken from the lime pits (usually wooden vats sunk in the ground) and thrown into a washing machine, where it is thoroughly agitated in a continuous stream of water until practically all of the lime is washed out, which may be determined by cutting open a piece of stock and testing the interior with litmus or phenolphthalein. The slight remaining alkalinity is neutralized by soaking in very weak acid. For very clear glues HCl is used, the resulting calcium chloride being very soluble; H_2SO_4 gives a precipitate of $CaSO_4$ which renders the glue more or less opaque. At this point sulphurous acid is often used to bleach and further plump the stock; alum is also used to bleach the stock and harden the jelly. After thorough draining the stock is transferred to the boiling tank or kettle.

The "cone washer" is the one most in vogue in this country; the heavy wooden cone kneads, presses and turns the stock, effectively loosening the lime which is carried away by a stream of water entering from a perforated standpipe at the center and flowing through perforated iron plates at the sides or bottom of the tub.

Fresh Bone is sometimes boiled without even a preliminary washing; but if washed and degreased (so-called benzine process) it yields a much clearer glue. Bones may be made into glue by the "sulphurous acid process" patented by Grillo and Schroeder, according to which bones are disintegrated by moist sulphurous acid gas or liquid SO_2 according to the equation:

$$Ca_3(PO_4)_2+SO_2+H_2O=Ca_2H_2(PO_4)_2+CaSO_3.$$

Bones thus treated readily dissolve in the kettle; any acidity is neutralized with milk of lime, and the resulting "mud" after the calcium sulphite is oxidized by exposure to the air or by oxidizing agents, forms a valuable fertilizer.

The Boiling Process. In the extraction (or cooking) of glue the prepared stock is subjected to the solvent action of hot water by which the collagen undergoes a change into glue. Hofmeister regards this process as a hydrolysis proceeding in two stages according to the equations:

$$\underset{\text{Collagen}}{C_{102}H_{149}N_{31}O_{38}}+\underset{+\text{Water}}{H_2O}=\underset{\text{Gelatine}}{C_{102}H_{151}N_{131}O_{39}};$$

$$\underset{\text{Gelatine}}{C_{102}H_{151}N_{31}O_{39}}+\underset{+\text{ Water}}{2H_2O}=\underset{\text{Semiglutin}}{C_{55}H_{85}N_{17}O_{22}}+\underset{+\text{ Hemicollin}}{C_{47}H_{70}N_{14}O_{19}};$$

but in dealing with substances of such variable composition, empirical formulæ of this kind have no great significance. Indeed the whole boiling process seems rather to be the gradual breaking down of colloid complexes with accompanying changes in the amount of absorbed water, and to consist of physical as well as chemical changes.

The higher the temperature, and the longer the stock is exposed to it, the more rapidly these degenerative changes proceed and the lower the test of the glue. Hence it is desirable to extract the stock as quickly and at as low a temperature as possible. Here again the differences in stock necessitate the use of different types of kettles, or cookers, which may be grouped into two classes: 1. Open tanks; 2. Pressure tanks.

Open Tank. The open tank usually consists of a rectangular or round wooden tub having a closed steam coil over which a perforated false bottom of wood or iron is placed so as to leave a circulating space between the two. Upon the false bottom is spread a layer of excelsior to serve as a rough strainer, and on top of this the stock is thrown to within a foot or so of the top. Sufficient clear water is then added to cover the stock, and steam turned into the coil; when the desired temperature is reached, the steam is cut down to the minimum needed to maintain it until a sufficiently concentrated " soup " or glue solution is obtained, which may be determined by chilling a sample in a small cup. After skimming off the floating grease, this solution, the " first run " as it is called, is drawn off for further treatment, the stock again covered with water and a second run made in like manner, the same process continuing as long as any glue is left in the stock. The last run or washwater is extracted at boiling heat and is usually so weak that it must be added to another kettle, or be mixed with a stronger preceding run or else be evaporated.

Hide, sinew or ossein stocks are the ones usually boiled in the open kettle, and as they are greatly softened by their preliminary liming, they disssolve at comparatively low temperatures. As a rule three or four runs suffice to exhaust the stock, the residue of which (glue manure or tankage) is then dried for use as fertilizer. The tankage may contain much fat or insoluble lime salts of fatty acids, in which event it is first boiled with H_2SO_4 to liberate the grease.

Temperature. The temperature of boiling must in any event be above that favorable to bacterial growth, and usually begins at about 70° C. (158° F.), gradually increasing with each successive " run." The time required for boiling a " run " varies from one or two to six or eight hours, depending upon the softness of the stock and the temperature used. Several new types of open tanks have been patented in which the water is caused to circulate through the stock by mechanical means (rotary pumps, etc.), the object being to hasten solution; but with the ordinary tanks the stock is not disturbed, or, at most, occasionally stirred with a long pole to open it up.

Pressure Tank. The pressure tank process of boiling glue is largely used with untreated bones. The tanks consist of vertical steel or iron cylinders capable of withstanding several atmospheres pressure, having convex ends and large manholes at the top for filling and at the bottom for discharging the steamed bone.

The bones may be boiled with water under pressure (10–20 lbs.), the water may be allowed to trickle in from above while steam enters below (English process) or the condensation of the steam may supply the necessary water (French process). The successive runs of glue obtained are more concentrated than by the open tank method, but as a rule do not have as strong a jelly; they are drawn off from time to time through a perforated false bottom. With fresh bones a large quantity of bone grease is incidentally produced.

Treating the Liquors. With ordinary glues, the liquors, concentrated in a vacuum evaporator if necessary, and preserved with antiseptics if desired, are run directly into galvanized iron pans or "coolers" where they set to a jelly, a process which frequently has to be assisted by artificial refrigeration if the boilings are weak or the weather warm. White or opaque glues are made by stirring in the desired quantity of oxide of zinc or other whitening material, before pouring the liquor into the pans.

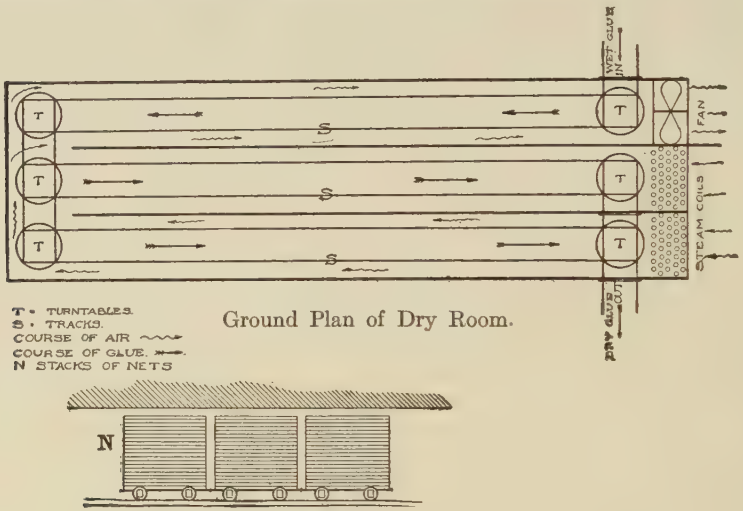
Clarification. Although ossein and calf stocks generally yield very clear liquors, in order to secure the extremely clear jellies required for some glues and food gelatines, both chemical and mechanical treatment of the liquors are resorted to. The chemical methods consist in forming within the liquor a flocculent precipitate which tends to absorb and carry down with it the turbidity-producing particles. Alum, phosphoric acid or sulphurous acid followed by milk of lime, and blood or egg albumen are among the substances thus used. After the addition of albumen, to produce coagulation the liquor must be heated, which has an injurious effect on its jellying strength. The treated solution is filtered through a filter press or a pulp or bone char filter, and then run into the pans.

Drying. The "coolers" or moulds are dipped for an instant into hot water to loosen the jelly blocks, which, by means of sharpened stretched wires operated by hand or arranged in special glue cutters, are sliced into sheets of any desired size and thickness. These jelly sheets are spread upon galvanized or linen nets, and high piles of the nets (called "stacks") are mounted upon wheeled trucks and are run into a dry room against a current of warm air which after passing over a large steam coil, enters the further end actuated by a circulating fan. Blower or pressure fans, and suction or exhaust fans are both used. See Fig. 368.

As the drying proceeds and the glue "skins over," it can be pushed nearer and nearer to the hot coil in front of which it gets its final "baking"; the stack is then withdrawn through a side door and the

finished dry glue taken from the nets to be broken, ground, and packed into barrels, bags or packets.

Drying frequently causes the manufacturer much concern, for weak jellies are apt to soften and stick to the nets or even run entirely through to the floor; and besides the fresh jelly is open to the inroads of bacteria whose action may result in black or offensive smelling glue.



Ground Plan of Dry Room.

Side view of one alley.

Fig. 368.

Grading. None of the so-called chemical tests for glue have any practical significance, but by experience it has been learned that glues made from certain stock and possessing certain physical characteristics give good results when used for certain purposes. The most important physical characteristics are the viscosity and the jelly strength of a solution of the glue, and in order to have some means of expressing these numerically arbitrary standards have been selected which cover the wide range of commercial glues and gelatines. The following table gives the viscosity and jelly strength of such standards, determined on solutions of 25 grams of glue in 100 c.c. of water.[1]

The standard viscosities were determined with a standardized pipette which permits the efflux of 45 c.c. of water 80° C., in exactly 15 seconds

To determine standard jelly strength the "shot" test was found unreliable, and a special instrument was devised. It consists of a brass cylindrical vessel supported like a gas tank by four vertical rods, against which it slides with almost frictionless roller bearings. This brass cup is allowed to rest on a truncated cone of jelly of definite size, composition, and temperature; and shot are gradually poured into the cup until

[1] See *J. Soc. Chem.*, Vol. XXV. p. 158 (1906).

a definite compression of the jelly is observed. Beneath the cup are two vertical adjustable brass uprights 3.5 cm. high, connected with an electric bell circuit; so that when the cup reaches their level, it completes the circuit and the bell rings.

Standard.	Viscosities (in secs.) at 80° C. solution 25–100.	Allowable variation of viscosities (in secs.).	Jelly strength (in ozs.) at 10° C.	Jelly strength (in gms.) at 10° C.
10	15½	±¼	—	—
20	16	±¼	—	—
30	16½	±¼	—	—
40	17	±¼	60	1701
50	18	+½	82	2324
60	19	±½	104	2948
70	20	±½	126	3572
80	21	±½	148	4196
90	22	±¾	170	4820
100	23	±¾	192	5443
110	24	±¾	214	6067
120	25	±1	236	6691
130	26	±3	258	7314
140	28	±5	—	—
150	34	±8	—	—
160	40	±12	—	—

The weight of the brass cup plus the weight of the added shot gives a figure which expresses the jelly strength.

The jellies are cast in brass cups 6 cm. high, 5.5 cm. in diameter at the open top, and 5 cm. at the bottom, which is closed with a tight-fitting external friction cap. The jellies are removed by dipping the cups for an instant in hot water, taking care that no material loss results. The liberated truncated cones should be 4.5 cm. high, the cups being filled only to that level. They are placed in a thermostat until they reach the required temperature, 10° C.[1]

Thin blown glasses about 8–8.5 cm. high and 5.5 cm. in diameter are convenient for tests. 25 grams of each glue to be tested is broken into small pieces and soaked in 100 c.c. of water until softened; and at the same time a number of standard glues, above referred to, are treated in like manner. All the glasses are at the same time placed in a water-bath, heated to 80° C., and stirred until a perfect solution is obtained. More or less than 25 grams per 100 c.c. can be used as long as the standards and unknown glues are all treated alike. The reaction is determined with litmus paper. In cases where the degree of acidity or alkalinity is desired, a separate titration is made.

Viscosity or Running Test. Keeping the temperature uniform, the viscosity is determined by running the hot solution from a pipette, noting

[1] The standard jelly tester and pipette are to be had of Eimer & Amend, New York.

the time of efflux by a stop-watch. The relative viscosities are thus fixed in seconds. After each determination, the pipette is washed with hot water, and care must be taken that no partially evaporated glue or slime clogs the outlet. While running, the pipette may be kept in a specially constructed thermostat. More complicated viscosimeters, as Engler's or the Rideal-Slotte instrument, may, of course, be used.

The *odor* of the hot solution is then noted and the glue rated as sweet or "off." Decomposition is readily detected, although it is often masked by phenol or ethereal oils. Besides, the smell gives some indication of the stock from which the glue was made.

Grease. The glue solution is painted on a piece of white paper with a little aniline or dry color, and spots of "eyes" appear roughly proportionate to the amount of grease present.

Foam. This is determined by agitating the solution with a rod or mechanical agitator. An egg-beater serves very well. Like grease, foam is estimated on a comparative basis.

Comparative Set. The glues are taken from the bath, allowed to cool, and the comparative set or speed with which the jellies harden is noticed.

Jelly Strength or "Test." When the jellies have reached the room temperature, the jelly strength or "test" is determined. For speed and perhaps also accuracy, we prefer the "finger test," and grade the jellies comparatively by pressure with the finger tips, the unknown glues naturally grouping themselves as stronger or weaker in jelly than the several standards. Notwithstanding the personal equation, expert operators obtain much more uniform results in this way than are given by the various mechanical devices.

Melting-point. The melting-point of the jelly as described by R. Kissling (*Chem. Zeitung*, 1901, 25, 264) is also of considerable value, for generally speaking, it is proportionate to the jelly strength. It may be determined by the simple apparatus described by N. Chercheffsky (*Chem. Zeitung*, 1901, 25, 413).

Strictly speaking, a glue jelly has no absolute melting-point, for it softens up gradually and shows no sharp line of demarcation between solid and liquid. Perhaps the best way is to put the test glasses back into the water-bath, and gradually raise the temperature, noting comparatively how the jellies melt.

Absorption Test. Schattmann (*Dingler's Polyt. Journ.*, 1845, p. 115) proposed as a means of valuation, to determine the percentage of water a glue will absorb under fixed conditions. The water absorption is usually in proportion to the jelly strength, which is the more reliable figure.

Binding or Adhesive Strength. For this there is no one test that can have a general application; the glue must be tried under actual working conditions. It stands to reason that if a glue is to be used to hold clay to paper, it is of small interest what its binding strength is on

mahogany, maple or porcelain blocks. Very often, in fact, a glue that will size paper perfectly will not make a joint.

Keeping Properties. The glasses are then allowed to stand uncovered at room temperature for several days to observe relative keeping qualities of the jellies. If the keeping property under special conditions is desired, these conditions are simulated.

As before suggested, these test figures must be read in the light of experience, and no one of them is sufficient to determine the value of a glue. The only test that can be accepted as conclusive is a practical trial of the glue under actual working conditions, which vary in each case.

Use. Glue is used for a multitude of purposes. Each line of work has its special requirements, and years of experience are necessary to pick out the right glue for the work. Trouble may be caused by a glue that is too strong as well as by one that is too weak. Although in using glue the most important thing is the selection of the right glue for the work, much depends upon its proper preparation and application. If anything that is glued up comes apart, the immediate verdict is "bad glue," which is often unjustifiable, for poor judgment or unskillful workmanship may be responsible.

In preparing glue for use the following points should be observed:

1. Use definite weights of glue and water. Glue is sold by the pound and should be used by the pound. 2. Soak the glue in cold water until it has thoroughly softened. Ground glue softens more quickly than sheet or flake glue, and is therefore preferable, other things being equal. 3. Melt in a water or steam bath, and keep at as low a temperature as is consistent with the work. Prolonged heating injures glue, so that it is advisable to heat up successive small lots of the soaked-up material, rather than have a large lot remain heated for a long time. 4. Make good evaporation from the glue-pot by the addition of water if necessary. 5. Use clean utensils. 6. Fit the strength of the solution to the work—don't use the glue too thick or too thin. 7. If surfaces are to be joined, have them dry and warm, if possible, and apply pressure until the glue has sufficiently "set."

Glues for particular purposes should be chosen as follows:

Wood Joints. Most preferable are hide glues from grade 70 up. Lower test hide glues may give trouble. While some bone glues answer admirably, in general they should be avoided. The pieces to be joined should be thoroughly fitted, dry, and of seasoned wood.

Veneers. Most advantageous is a bone and hide, or bone and sinew mixture, testing between grades 50 and 70. Higher test glues are apt to set too quickly. Pure hide or sinew glue is better, but more expensive, while, for cheap large surface work, bone glue may be used. If worked on a veneering machine, freedom from foam is essential.

Sizing. As most sizing is done with special machinery, each case must be considered individually. Generally a free-flowing glue, free from foam,

is required. If used to surface paper, grease is undesirable, as is any marked acidity or alkalinity which might turn the shade of the colors with which the size is mixed.

Paper Boxes. For "setting up," quick-setting hide glues, grades 70 to 90 are best. For "covering," lower test is necessary to prevent the glue setting too quickly; bone glues, testing grades 40 to 60, are most desirable. Of course, to the relatively higher test glues more water can be added; consequently they go further, and it is only a matter of proportion between strength and cost to determine the value.

Leather Goods and Belting. Here the main points are flexibility, tenacity, and resistance to moisture. Nothing under grade 100 should be used, and higher test goods are to be recommended, because they are less sensible to moisture, and interpose less mass between the surfaces joined. Fish glue, once largely used, is in disfavor, being too hygroscopic. Most leather-belt manufacturers make their own special "cement," using high-grade glue or gelatine as a base, and mixing it with glycerin and other ingredients.

Bookbinding. For rounding and backing, hide glues testing between grades 80 and 100 serve very well. If brittle low test or bone glues are used, the books are apt to crack down the back. Where simple pasting work is to be done, any sweet low-grade glue will anwer.

In all cases especial machinery demands glue suited to its particular requirements.

Gelatine. Only high-testing sweet glues made from selected clean stock under sanitary conditions, and free from objectionable chemicals, should be sold as gelatine to be used for food purposes. Gelatine is a very valuable addition to the dietary, as the use of calf's-foot jelly for invalids would indicate, for it facilitates digestion and conserves the body's nitrogen. Being a typical reversible colloid, it is used in small quantity in marshmallow confectionery, to prevent the crystallization of the sugar; and in ice cream, besides preventing grainy crystallization, it inhibits the curding of the casein (an irreversible colloid) thus enhancing the digestibility of both the casein and milk fat. It has in fact been recommended as an addition to infants' milk.[1]

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Regarding certain technical uses of glue and gelatine, see "Colloid Chemistry and Some of its Technical Aspects," *Journal Soc. Chem. Ind.*, Vol. XXVIII, p. 280 (1909).

[1] See *Zeitschrift für Chemie und Industrie der Kolloide*, Vol. V, p. 101 (1909); also *Jour. Am. Med. Assoc.*, Vol. LV, p. 1196 (1910).

CHAPTER XLIX

CASEIN

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Casein belongs to that great family of nitrogenous organic compounds called proteins. It is a very complex colloidal substance found in the milk of mammals and in the juices and seeds of certain leguminous plants. In the modified form of cheese, casein from the milk of cows and goats has been used as a food from the earliest times, but its chemical composition and manifold uses in the technical world were not known till recent years.

Casein exists in milk in the form of a colloidal suspension or emulsion not in the free state but in combination with calcium. Hammarsten, who first investigated this substance, called it calcium caseinogenate. He used the name caseinogen for the protein complex as it existed naturally in milk and casein for the precipitated or coagulated substance. English chemists, however, adopt a somewhat different nomenclature. The substance precipitated from milk by the action of rennet is called casein, which is equivalent to the American paracasein, while that precipitated by acids is called caseinogen, which is identical with the American casein.

Investigations by means of the ultramicroscope have shown that the fat globule of milk is surrounded by a membrane filled with innumerable particles of calcium caseinogenate in suspension. These together with calcium phosphate emulsifies the fat globule.

The casein molecule consists of six elements: Carbon, 52.96 per cent; hydrogen, 7.04 per cent; nitrogen, 15.6 per cent; oxygen, 22.78 per cent sulphur, 0.8 per cent; phosphorus, 0.82 per cent. The above per cents must be considered as averages. Hammarsten gives the following formula for casein, viz.: $C_{172}H_{274}N_{44}SPO_{55}$. The inner grouping of these elements is still unknown.

Chemistry. Casein can be precipitated from milk or other solutions by the addition of very dilute acids in slight excess. This is the only method of obtaining it in the free state. There are certain other precipitants, but in this case the casein is obtained in a modified form, either in combination with the precipitant or as the original calcium caseinogenate. Solutions of the salts of the heavy metals precipitate the corresponding salt of casein with that metal. Saturation with neutral salts or alcohol gives a precipitate of calcium caseinogenate, while aniline dye-

stuffs or alkaloids form complex compounds. These precipitants are not used except in cases where that particular compound is desired as the end product. Certain enzymes precipitate casein from milk, but the product is still further modified, often with a partial cleavage of the protein molecule.

The addition of dilute acids decomposes the calcium caseinogenate with the formation of the calcium salt of the acid and the precipitation of free casein. There is considerable evidence, however, that the casein salt of the acid is first formed and then this is broken down into free casein by the water present. The addition of enzymes is more complicated. Rennet precipitates cheese, which is not free casein, but the calcium salt of a cleavage product of the casein molecule called paracasein. This enzyme is obtained chiefly from the gastric mucosa of calves. According to some authorities it will not act except in the presence of soluble lime salts, which ordinarily occur in sufficient quantities in milk. Hammarsten considered that the action of rennet takes place in two stages: First, the enzyme splits the casein molecule into two parts soluble casein and whey protein; then the calcium from the calcium salts in solution unites with the soluble casein and forms an insoluble curd of calcium paracaseate, while the whey protein goes into solution.

Van Slyke and Bosworth, however, claim that rennet splits casein into two molecules of paracasein, which unite with the calcium present and form a precipitate of calcium paracaseate. The same authors claim also that the presence of soluble lime salts is not essential to the action of rennet, but that the whole phenomena of coagulation hinges on the fact that the alkali salts of paracasein are soluble in water while the alkali earth salts are not.

Casein is readily soluble in dilute aqueous solutions of the caustic alkalies, the normal and acid carbonates of the alkalies and alkaline earths, and in moderately strong acids. It is very easily broken down into simpler compounds (hydrolysis) if the above solvents are used in excess. The most recent determination of the molecular weight of casein (Van Slyke and Bosworth) places it at 8888± while that of paracasein is 4444±. It is practically insoluble in alcohol, ether or water. It is at least a tetrabasic acid, and like nearly all other compounds which contain the amino group, it can act also as a base. The salts with the alkali bases can be obtained as dry powders by the evaporation of their solutions. The following salts of casein with bases have been prepared; Ca, Na, K, NH_4, Cu, Mg, and Hg. All soluble salts of casein can be rendered insoluble by treatment with formaldehyde, with soluble chromates and subsequent exposure to light, or with hexamethylenetetramine In the dry or moist condition it is very susceptible to high temperatures. Its solutions are not coagulable by heat, are levorotatory to polarized light and those of the alkalies can be boiled without alteration. When solutions of casein with the alkaline earths are heated above 40° C. a precipitate is

formed. This phenomena is not one of coagulation in the strictest sense, but is due to the formation of an insoluble salt of the base. The liquid at the same time becomes more alkaline.

Occurrence. Casein exists in cow's milk to the extent of about $3\frac{1}{2}$ per cent and forms 80 per cent of the entire protein content. Commercial casein is prepared almost exclusively from cow's milk. In Europe goat's milk is used to a considerable extent and in India the milk of the buffalo.

The casein industry as such originated in the United States and within the last twenty-five years has reached enormous proportions. The domestic supply is not equal to the demand and large quantities are imported from Europe and South America.

Preparation of Technical Casein. One of the principal requirements of technical casein is freedom from fats. To this end sweet milk is put through a centrifugal cream separator and then 4 to 6 per cent of caustic alkali in solution (or better, 10 per cent of sodium bicarbonate) is added. The amount of alkali is based on the casein content of the milk. The solution is slightly warmed, and put through the separator several times again. This procedure removes practically all the fats. The milk is run into a vat and dilute sulphuric or hydrochloric acid is added by degrees and the mixture constantly stirred. Small portions are taken out from time to time and tested until precipitation is complete. After precipitation the curd is allowed to settle and the supernatant liquid siphoned off. The curd is stirred up with cold water, allowed to settle again and the water siphoned off as before. This is repeated until the effluent water is perfectly clear, and neutral.

The curd is then placed on cheesecloth filters, or on a sloping table and allowed to drain. Next it is put into strong cloths and pressed in an ordinary cheese press until no more water comes away. The curd must then be dried, and in order to facilitate this process it is necessary to break it up into very small pieces. This is done by a curd mill in which the curd passes between toothed rollers. Since casein is very susceptible to heat it must be dried at a very low temperature. This is accomplished in several ways. One of the best methods is by means of the vacuum dryer, which consists of a steam-jacketed outside cylinder and a concentric revolving inside drum, heated by live or exhaust steam. To the inside drum stirring blades are attached. The casein is dried between the inside drum and the outside cylinder, and is kept in constant motion by the stirring blades. After charging the apparatus, the manhole is closed and a high vacuum produced by means of an air pump, the vapors passing into a condenser.

Another vacuum dryer consists of a steel vacuum chamber with rubber shod doors. The requisite temperature is obtained by means of a coil of pipe filled with hot water or steam and placed around the inside chamber. The well-pressed casein is placed on trays made by stretching

cheesecloth over wooden frames. These trays fit into grooves on the inside of the vacuum chamber.

In some factories the fine curd is dried by feeding it into a revolving steel drum which is enclosed in another stationary one. The space between the two drums is filled with hot water. The entire apparatus is set on an incline so that the curd which is fed in at the upper end will pass through the drum as it revolves, and finally emerge in a well-dried condition at the other end. After being placed in sacks or barrels the dried casein is ready for shipment.

Well-dried casein will keep indefinitely if properly protected from moisture. Since some of the bacteria from the milk must inevitably find their way into the casein, or outside bacteria contaminate it, the least amount of moisture will start decomposition. Some manufacturers sprinkle a few centimeters of alcohol into each container, if a tight one. The alcohol vaporizes gradually and inhibits the growth of bacteria. Ordinarily casein is a perfectly white ashless, hygroscopic powder, but under certain conditions it can be made in the form of glassy transparent grains.

Casein from Buttermilk. Of late years numerous attempts have been made to utilize the casein from buttermilk. It has been found, however, that the souring of the milk and the decomposing action of the bacteria change this casein very materially. Hydrolysis occurs to a certain extent, considerable ammonia is given off and concurrent oxidation takes place. The casein residue becomes less soluble, yellow in color and loses considerable of its adhesive character. This renders it unfit for the more important technical uses. In addition it is almost impossible to remove the last traces of butter-fat from it which fact alone prevents its use in processes where the other defects are not so objectionable.

To obtain casein from this source, the buttermilk is heated, the coagulated curd filtered off and then treated in exactly the same manner as sweet milk casein. Owing to the finely divided character of this casein considerable difficulty is experienced in separating it from the whey. It is also liable to spoil before drying is complete.

Examination and Analysis of Technical Casein. In addition to the content of pure casein, the physical properties of the product such as fineness of powder, solubility, color and condition (sweet or sour) are of considerable importance. An average analysis of a good grade of technical casein is as follows: Water, 9.23 per cent; casein, 85.50 per cent; fat, 0.85 per cent; ash, 4.07 per cent; nitrogen, 13.6 to 14.0 per cent.

Moisture is determined by weighing out 5 grams of casein into a nickel dish and heating it in an oven at 100 to 105° C. to constant weight. One to two hours' heating should be sufficient.

Nitrogen is determined by the Kjeldahl method. One-half gram of casein is digested with 25 cc. concentrated sulphuric acid and 5 grams of anhydrous potassium sulphate. A drop of mercury is added as a catalyzer. The ammonia is distilled into 25 cc. half-normal sulphuric acid

and the excess acid titrated back with half-normal sodium hydroxide. Congo red is used as indicator.

Casein is computed by multiplying the percentage of nitrogen by the factor 6.38.

Ash is determined by burning 2 grams of finely ground casein in a platinum dish. The residue is dissolved in water and a small amount of a solution of ammonium nitrate added. It is then evaporated to dryness and heated to low redness, cooled in a desiccator and weighed.

Free acid is determined by shaking 10 grams of casein with 100 cc. of distilled water. It is allowed to stand for several minutes and then filtered; 50 cc. of the filtrate are titrated with deci-normal sodium hydroxide, using phenolphthalein as indicator.

Solubility is determined by weighing 10 grams of air-dried casein into a beaker, and pouring over it 50 cc. of water containing 2 cc. 33 per cent ammonia. It is heated to 60° C. and allowed to stand one hour with frequent stirring. Pure casein should completely dissolve.

Technical Applications of Casein. The colloidal character of casein renders it especially useful as an adhesive. The true solutions of casein are not colloidal, and consequently are neither adhesive nor viscous. To attain this end the amount of alkali used must not be quite sufficient to dissolve the casein, i.e., to make a true solution. In this case the casein is not all dissociated, but the entire mass is rendered extremely colloidal. The adhesive qualities can be imparted to casein solutions by the addition of tannin, or some alkali tannate, e.g., calcium tannate. The use of tannin, however, is not satisfactory, because of the discoloration produced in the solution by the action of the tannin on the iron salts, which are always present to a very small amount, either in the casein or in the water used.

Preparation and Application. Dried casein is soaked in an equal weight of water for two hours. The casein swells up but does not dissolve. At the end of that time 14 per cent of borax in a hot saturated solution is added and the mixture stirred continuously till solution is complete. A thick mucilagenous dough results which can be thinned down to any desired consistency with hot water. Sodium bicarbonate, sodium tungstate, ammonia or the caustic alkalies can be used in place of borax. Sodium silicate and lime are best when a cement for porcelain, metals or stoneware is desired. Calcined magnesia produces a quick-hardening cement. The adhesive properties can be increased by the addition of a little sodium arsenate, and a small amount of camphor will effectually prevent the ravages of insects.

These glues are put on the market in two forms, first in a dissolved condition ready for use, second, as a dry powder in which the requisite amount of casein and alkali are ready mixed. In the latter case it is only necessary to add hot water to the powder, stir till dissolved and then thin down to the desired consistency with hot water. In the wood-working

and cardboard industries the casein glues are superior to the ordinary adhesives. They are inodorous and gradually harden and become insoluble. Bottle labels and the like when moistened with formaldehyde, dried and coated with casein will effectually resist moisture. If a putty is desired it is only necessary to add powdered lime and knead until a thick dough is secured. This hardens very quickly and serves all the purposes of putty.

Casein in the Paper Industry. The paper industry offers an ever-widening field for the use of casein. The utility of paper itself and all substances made from it, or wood pulp, owe their increased utility to some of the peculiar qualities imparted to them through the medium of casein solutions. Cardboard, paper flasks, buckets, bags, and wrapping paper can be made waterproof by impregnating them with casein solution and subsequently exposing them to formaldehyde vapors. Paper bottles can be made sterile and impervious to moisture, milk, oils and other liquids by the same process. Wallpaper can be made antiseptic. Paper slates and drawing paper can be made erasable by coating them with casein solution to which finely divided magnesia or lime has been added. The sizing or enameling of paper in this manner has reached remarkable proportions. In this industry casein glue is used as a binder for the enameling substance and as a fixing agent for the colors.

Preparation and Application. Borax or soda casein is diluted down to the right consistency with hot water and finely powdered china clay, kaolin or chalk together with the desired coloring matter. This mixture is thoroughly incorporated together and placed in a vat. The paper to be coated is made to pass in an endless chain through the vat and a small amount of this prepared mixture is transferred to the paper by a fine brush. The sheet then passes between other brushes which scrub the coating into the interstices of the paper and at the same time remove any excess. Next the paper passes through a drying chamber, where it is partially dried, and at last between heated rollers, which press the coating into a hard smooth finish.

Casein Paints. Casein combines with certain substances to form agglutinant compounds which are very stable and extremely resistant to moisture and other atmospheric changes. They all become more or less insoluble on exposure to air. In addition it forms compounds with coloring pigments, aniline dyestuffs and certain substances used for subtrates. These properties render a solution of casein mixed with coloring matters especially useful as a paint or varnish, in which case the alkali solution of casein takes the place of linseed oil. Both basic and acid aniline dyes can be precipitated on any substratum by casein. Paintings executed on canvas with casein colors will resist atmospheric changes for years. They show remarkable brightness of colors and a splendid velvety sheen. They can be rendered waterproof by formaldehyde and are easily cleaned.

These paints are generally used as a thin liquid or paste in which the

casein exists in a partially dissociated condition. They are similar to water color paints in that they dry very quickly and without gloss. The surfaces to be painted do not need any special preparation, although all previous applications of oil paints must be removed.

Preparation and Application. Casein paints consist of an alkaline solution of casein together with a suitable filler and color pigment. The binding medium is made by dissolving casein in an aqueous solution of caustic soda, borax, sodium bicarbonate, ammonia or sodium silicate. A small amount of an aqueous solution of soap, wax or rosin is sometimes added in order to protect the fine particles of coloring matter from atmospheric influences, and a few cubic centimeters of formaldehyde or phenol to render the casein antiseptic and to prevent the growth of molds and bacteria. For frescoing and inside ornamental work kaolin, china clay, lime or powdered feldspar is added as a filler and to give bulk and covering power. For artists' canvas the dissociated casein is emulsified by oils or fats so that the natural color of the pigment will not be altered by the binding medium. The addition of glass fluxes and metallic oxides produce an enamel-like finish and asbestos or diatomaceous earth gives a fireproof coloring. For outside work on buildings, etc., the media must be incorporated with quickline or cement, both of which form insoluble compounds with casein upon drying.

The next step is to mix one of the above media with the desired pigments. It is absolutely necessary that the pigment be indifferent to the alkali used. The pigments most suitable for white are, baryta, white lead, china clay, lithophone, or zinc white; for red, carmine, Indian red, or vermilion; for yellow, cadmium yellow, Naples yellow, or yellow ocher; for black, ivory black or lamp black; for blue, cobalt blue, indigo or ultramarine; for green, chrome green, cobalt green or emerald green.

The proportions of binding medium, filler and pigment vary according to the nature of the work. When these paints are intended for shipment and use at a distance the above ingredients, in a dry condition, are mixed together in the proper proportions, ground to a fine powder in a paint mill and packed in tight containers. This mixture will keep indefinitely if protected from air and moisture. It is made ready for use by adding 50 parts of water to every 100 parts of the powder and allowing it to stand for some time. The alkali dissolves in the water and in turn acts as a solvent for the casein. The mixture is then thoroughly incorporated by repeated stirring and thinned down to the required consistency with hot water. The paint is then ready for use, and can be applied in the same way as oil paints, the only necessary precaution being to keep the mixture thoroughly stirred. These paints will adhere to almost any surface and will set very hard in a short time.

Plastic Masses from Casein. Casein is analogous to other compounds having strong adhesive qualities in that a great variety of plastic masses can be made from it, either alone in the form of a fine powder, or in an alkaline

solution together with admixtures of other substances, such as paper, bone dust, powdered stone, etc. These mixtures possess the property of becoming very plastic under the influence of heat and in this condition they can be kneaded, rolled, pressed or molded into any desired shape. They dry very quickly, are non-inflammable and do not shrink on drying provided an excess of water is avoided in the process of mixing. Any desired color can be added or transparent horny masses obtained. Articles made from these mixtures can be turned in a lathe, or shaped by any other cutting tool, and when finished take a fine polish.

Preparation and Application. If casein is used alone it is preferable to use the moist curd. This is heated to 175° F., and kneaded till a homogeneous mass is secured. It is then pressed or molded into the desired shape and very carefully dried. If it is desired to incorporate other substances, the alkali solutions of casein are preferable. In this case it is necessary to partially precipitate the casein with acids or salts in order to obtain the maximum plasticity. Other substances, such as powdered feldspar and pigments, are added and the mass treated as in the case of the moist curd. Plates or ornamental designs of the above are used for paneling or inside decorations. For chessmen, toys, etc., the addition of strontium hydroxide and powdered marble give articles of exceptional hardness and durability.

In Germany great progress has been made in the manufacture of celluloid articles from an admixture of casein and celluloid, or casein and cellulose or nitrocellulose. For this purpose casein and cellulose are dissolved separately in acetic acid and then mixed together and carefully evaporated. The inflammability of celluloid itself can be diminished by the incorporation of a small amount of casein with it.

The greatest achievement along this line, however, is galalith, a substance made from casein, either in an alkaline solution or in the dry powdered state. This is rendered colloidal by a small amount of acids or salts, and after kneading to a homogeneous mass and molding, it is very carefully dried and rendered insoluble by formaldehyde. It is harder than celluloid, a non-conductor of electricity, inodorous and non-inflammable. It can be rolled into thin sheets or thick plates and used in place of mica on electrical instruments.

Other substances, akin to the above, such as imitation leather or linoleum, can be made by impregnating a mass of vegetable fibers or animal hair with a mixture of oil, turpentine, glycerine and casein glue. This is partially dried and treated with aluminium acetate, after which it is thoroughly pressed between heated rollers. By pressing several sheets together a leather of any desired thickness can be secured. A mixture of casein, vegetable oil, caoutchouc or rosin gives a substance which is one of the best electrical insulators known.

Uses of Casein in Dyeing and Printing Textile Fabrics. When textile fabrics are impregnated with a solution of casein, the fiber becomes coated

with a thin layer of casein which materially increases the absorption of the dyestuffs of the bath. It thus acts as a mordant for the colors. When used alone it acts as a loading or softening agent for silk and cotton goods and renders the cloth more impervious to water. At first only the alkaline solutions of casein could be used, but recently it has been discovered that under certain conditions the dye bath should be made acid without precipitating the casein.

Preparation and Application. The general method consists in soaking the fabric in the casein solution and then passing it through the dye bath. Afterwards the fabric is dried and the coating rendered insoluble by exposure to the vapors of formaldehyde, or by dipping it into a solution of aluminium acetate. Another method is to incorporate the dyestuffs with the casein solution and complete the operation of mordanting and dyeing in one bath. The addition of glycerine solutions to the above bath renders the fabric more flexible and increases the gloss. Finely divided coloring matters impart a metallic luster to the cloth, while soap increases its softness. After treatment with formaldehyde the tone of the colors remain as pure as those fixed with egg albumen.

A solution of casein in lime water is used under the name of caseogum. Argentine is a compound of casein with zinc and gives a metallic luster to the fibers. Glutin is a solution of casein in sodium tungstate.

Casein as a Food. From time immemorial casein in the modified form of cheese has been used as a food by humanity. Casein itself is somewhat indigestible, but several of its compounds with the alkalies are very soluble in water and consequently are readily acted upon by the digestive juices. Recently several new compounds have been put on the market for this purpose, but the cost of production has prevented a wider use.

Preparation. The alkali salts of casein are used almost exclusively in these foods. They are made by the evaporation of their solutions and are put on the market in the form of dry powders. They are very nutritious and inodorous, and if kept dry will keep indefinitely. Several of them have different proportions of milk sugar and butter-fat added in order to increase their nutritive qualities. With the exception of cheese none of them are important as yet and consequently only a few of them are enumerated below.

Lacterine is one of the best known; it is a white powder composed of casein and a small per cent of mineral and non-nitrogenous matter. Nutrose is sodium caseate; plasmon, potassium caseate, and eucasein, ammonium caseate. Sanatogen is a compound of casein with sodium glycerophosphate. Synthetic milk is made from casein, sodium bicarbonate and a mixture of butter-fat and milk sugar. Flour and casein give a bread low in carbohydrates and find a use in certain dietary foods. A baking powder is on the market consisting of casein and calcium phosphate.

Casein in Medicine. The caseates of iodine, chlorine, mercury,

iron, silver, arsenic, phosphorus and a large number of alkaloids and organic compounds are used in medicine to an ever-increasing extent. The casein iodides are especially valuable. These compounds are used in intestinal disorders and certain skin diseases. The casein complex increases the adsorption of the iodine by the organism. The case in salicylates are readily absorbed by the intestines and do not irritate the mucous membranes as do the other salicylates. When combined with alkaloids the casein residue seems to tone down the harmful effects of the drug without materially affecting the specific action desired. It is said that three times as much mercury can be administered in the form of the caseate to a dog or rabbit without causing death as can be given in the form of the sublimate.

Preparation and Application. The salts of the metals are made by treating an alkaline solution of casein with a solution of a salt of the metal. The halogen compounds are prepared by treating an alkali solution of casein with the gaseous halogen, or with an alcoholic solution of the same; while the casein compounds of casein with the alkaloids are obtained by treating a suspension of casein in alcohol with an alcoholic extract of the alkaloid.

Sodium caseate in a thick paste is used as an ointment. Mixed with a small amount of formaldehyde and applied to a cut or bruise it forms an elastic coating " new skin " over the injury and absolutely prevents outside infection by bacteria or other agency.

Sundry Uses for Casein. In addition to the foregoing there are other uses, which, though important, are not so extensively used. A few of the other industrial uses are as follows: In soap making, in priming artists' canvas, as a paint remover, shoe polish, photographic plates, roofing pulp, massage cream, artificial silk, and as an agent for solidifying mineral oils.

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CHAPTER L

PRACTICAL APPLICATIONS OF COLLOID CHEMICAL PRINCIPLES

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The practical applications of colloid chemistry are so manifold and widespread that they touch every branch of science and technology. Whole books may be and have been written on many of the most restricted fields, while the scientific literature teems with monographs and articles, directly on, or applicable to, colloid-chemical subjects. In what follows, it will be possible therefore to give not an exhaustive, but only a most general survey, intended rather to show the ubiquity of colloid phenomena; and many important topics must be dismissed with a most rudimentary discussion, entirely unworthy of their importance.

Astronomy. As matter in colloidal state is so common on our relatively minute earth, it is but natural to expect to find many instances of colloidal dispersion in the immensity of the Universe.

Cosmic dust is widely distributed throughout the space, and as it is gathered by the superior attraction of the larger heavenly masses (suns, planets, etc.), which in any system grow at the expense of the smaller masses, fresh quantities are continually being produced by the collisions of bodies in space, as well as the disintegration of meteorites, comets, asteroids, etc.

The tails of comets seem to consist almost entirely, and the nuclei and coma largely, of colloidally dispersed matter. The great comet of 1882 which made a transit of the sun, was invisible against the solar disc (a position corresponding to attempted observation of colloidal particles in the ordinary microscope against a luminous background), but became visible again after passing beyond the sun's disc (a position corresponding to successful observation of the same collodial particles in the ultramicroscope against a dark background, the eye of the observer being protected from the source of illumination).

The streaming of the cometary tails away from the sun may be due to the ionization of the constituent colloidal particles and their consequent electrical repulsion; or more probably it may be due to the sun's rays, as was pointed out by J. Clerk Maxwell. The intensity of the action of the sun's rays on a particle depends upon its *surface*, which varies as the *square* of its diameter, whereas the gravitation of the same particle to the sun depends upon its *mass*, which varies as the *cube* of its diameter.

Theoretically in the case of a particle whose density equals that of water, the repulsion balances gravitation when the diameter reaches 0.0015 mm ($=1.5\mu$). As the diameter diminishes the repulsive force gains the ascendancy soon reaching a maximum and again diminishing until when the particle has a diameter of only 0.00007($=70\mu\mu$) the two forces again balance each other.[1]

These figures, which refer to a substance having the density of water, approximate colloidal dimensions; but in the case of denser bodies the subdivision would be even more profound. It is therefore not surprising that, when the earth recently passed through the tail of a comet, no disturbance of any kind was noticed. The comet's tail is a vast celestial camouflage—its luminosity a macroscopic Faraday-Tyndall effect.

The nebulæ, too, apparently consist of finely dispersed matter, rendered luminous by neighboring suns; although with them as with the comets a small part of the light may result from self-luminescence (incandescent gas, etc.).

Meteorology. What we commonly call "weather conditions" are largely dependent upon the degree of dispersion of water in the atmosphere, and this dispersion is mainly effected and maintained by solar heat and electrical energy. When air carrying water vapor is chilled by rising to a higher level, meeting a colder mass of air, or even by the alternation of night and day, the moisture it contains assumes the colloidal state as cloud, fog, or mist; and as the coagulation of the dispersed water proceeds, these in turn may condense still further into dew, rain, snow or hail, depending upon conditions. When the dispersed water aggregates, there is naturally set free the energy originally used in its dispersion. And this may appear as electricity (lightning) especially if the aggregation occurs suddenly as is the case in thunder and hail storms. We have all noticed how a nearby lightning flash is promptly followed by an increased fall of raindrops.

Were it not for our atmosphere the sun would appear to us like a fiery ball set in a black star-sprinkled sky. The blue color of the sky is due to diffraction of the sunlight by the earth's atmosphere, a gigantic Tyndall effect. If we look edgewise through a clear sheet of glass, we at once notice the green color due to colloidally dispersed iron, and in like manner, if we look through a great length of the atmosphere the prevailing color is blue. As the poet Campbell beautifully puts it:

> "'Tis distance lends enchantment to the view,
> And robes the mountain in its azure hue."

After the tremendous explosive eruption of the volcano Krakatoa in 1883, colloidal dust and ashes were projected so high that they gradually spread around the earth, causing "golden sunsets."

[1] See Simon Newcomb's article on "Comet," Encyclopædia Britannica, 11th ed.

Geology and Minerology. The ordinary properties of the solid constituents of the earth's crust depend more upon their state of physical subdivision than upon their chemical constitution. Atterberg classified the fragments of minerals and rocks as follows:

	Diameter.
Boulders	2 m. to 20 cm.
Pebbles	20 cm. to 2 cm.
Gravel	2 cm. to 2 mm.
Sand	2 mm. to 0.2 mm.
Earth	0.2 mm. to 0.02 mm.
Loam	0.2 mm. to 0.002 mm.
Clay	smaller than 0.002 mm.

The smaller the particles, the greater their capillarity and the ease with which they are moved by wind and by water, but the less their permeability to water. Fine deflocculated clay is carried thousands of miles by rivers until it is finally coagulated by the salts of the ocean, as may be observed in the deltas of the Ganges, Nile and Mississippi. Fine particles are easily cemented by pressure or igneous action into rocks (e.g., sand-stone, slate), or may act as a cement for large particles (e.g., pudding-stone) or as a matrix for fossils.

Many minerals are themselves colloidal gels (e.g., opal, flint, bauxite) or result from the weathering of other minerals with consequent gel formation (e.g., kaolin from kaolinite, serpentine from diabase). Most gems owe their colors to impurities colloidally dispersed within them (e.g., ruby, emerald, amethyst). Dendrites are formed by solutions diffusing through mineral gels. Colloidal minerals usually adsorb, and are dyed by aniline dyes (methylene blue), whereas crystalloid minerals are unaffected.

Clay and Ceramics. The effect of vegetable extractive matters on the working properties of clay have been known from ancient times; in the Bible (Exodus v) it is mentioned that brick cannot be made without straw. Recently patents have been taken out for "Egyptianizing" clay by adding to it tannin, extract of straw, humus and the like. Glue and similar protective colloids deflocculate or "free out" clay and make it "cover" in paper-coating and kalsomining. The working properties of clays depend largely upon the size of their constituent particles and their state of aggregation. This is especially evident in the manufacture of ceramics. Articles molded of clay and then burned lose their hydrosol condition and become hardened into pottery.

Agriculture. Although from time immemorial farmers have classified soils on the basis of their physical and physiological character as "light" or "heavy," "rich" or "poor," "productive" or "unproductive," etc., it is only within comparatively recent years that chemists have begun to realize the full importance of the role played by the colloids, especially the organic colloids of the soil.

Many important properties of soils, such as permeability, capillarity, absorption, moisture content, etc., are dependent not so much upon the chemical composition as upon the size of the constituent soil particles.[1] In coarse sand, for example, the amount of water is greatest at the bottom and smallest at the top, whereas in fine clay the distribution is much more uniform.

Among the natural agencies tending to increase the size of the minute soil particles may be mentioned heat with its drying or evaporative effect, freezing, and the coagulating or flocculating action of soluble inorganic salts and some organic substances present in the soil. On the other hand, included in that little known class of substances vaguely described as "humus" there are numerous organic substances derived from bacterial, plant, or animal debris, or exuded by the roots of plants, which act as protective colloids (Schutzkolloide) and tend to produce and maintain the hydrosol, or deflocculated condition.[2] In an excellent paper on the mechanics of soil moisture, L. J. Briggs[3] pointed out that very small quantities of certain organic substances such as are continually being produced in the soil by the decay of organic matter, greatly decrease the surface tension of solutions, thus counteracting to a large extent the effects of the surface application of soluble salts which would tend to draw moisture to the surface by increasing the surface tension of the capillary water of soils. It is well known, however, that an excess of salts will ruin a soil physically, as is evident after flooding by sea-water or the continuous application of chemical fertilizers. Of interest in this connection is the recent work of the Bureau of Soils, U. S. Department of Agriculture, carried out by Cameron, Schreiner, Livingston and their coworkers. Thus plants grown in the unproductive Takoma soil were greatly benefited by green manure, oak leaves, tannin and pyrogallol. The injurious effects of quinone and some other organic substances may be due to their ability to precipitate or flocculate the protective colloids of the soil; for as Lumière and Seyewetz have shown[4] quinone renders gelatin insoluble.

The fact observed by Fickenday[5] that more alkali is required to flocculate natural clay soils than kaolin suspensions, he attributes to the protective action of the humus present.[6]

A. S. Cushman, in his excellent work upon the use of feldspathic rock as fertilizer[7] has shown that the fine grinding of feldspar increases the

[1] Atterberg, Schwed. landw. Akad., 1903, and Chem. Zeit., 1905, 29, 195; Patten and Waggaman, U. S. Dept. of Agri. Bureau of Soils, Bull. No. 52, 1908.

[2] P. Ehrenberg, "Die Kolloide des Ackerbodens," Zeits. angew. Chem., 1908, 41, 2122.

[3] U. S. Dept. of Agric. Bureau of Soils, Bull. No. 10, 1897.

[4] Bull. Soc. Chem., 1907, 4, 428–431; J.S.C.I., 1907, 703.

[5] J. Landw., 1906, 54, 343.

[6] Keppeler and Spangenberg J. Landw., 1907, 55, 299.

[7] U. S. Dept. of Agri. Bureau of Plant Industry, Bulletin No. 104; Cushman and Hubbard, J. Am. Chem. Soc., 30, 779.

amount of potash available under the action of water. Thus, a coarse powder having an area of 43 sq.cm. per cc. of solid feldspar yielded 0.013 per cent, whereas a fine powder whose area was 501,486 sq.cm. per cc. yielded 0.873 per cent of potash and soda. These fine particles averaged about 0.1μ in diameter, which is relatively large as compared with colloidal dimensions; but under the action of physical and chemical soil agencies they undergo further disintegration, finally reaching a colloidal condition in which still more of their potash is available, a condition favored and maintained by the organic protective colloids of the soil.

With these brief and inadequate remarks we must dismiss this subject of such vast importance and fascinating interest, referring to the extensive literature, much of which is quoted in Bulletin No. 52 and the other publications of the Bureau of Soils.

Electroplating and Electrodeposition of Metals. As might well be expected the addition of protective colloids to electroplating baths tends to the production of fine grained non-crystalline deposits. A. G. Betts in a paper entitled "The Phenomena of Metal Depositing" [1] has shown that there are many factors influencing the action of the colloid, and has suggested a number of possible explanations. The correct explanation, however, has been given by Muller and Bahntje, [2] who state that the added colloid keeps the deposited metal (copper) in an amorphous, non-crystalline condition, gelatin producing the most powerful effect, egg albumen considerably less, while gum and starch have comparatively little action. They also found that the deposited copper weighed 0.2 per cent more than under normal conditions, indicating that some of the colloid had been carried down with the metal.

The relative efficiency of the colloids just referred to, corresponds to their relative efficiency in protecting from coagulation solutions of colloidal gold, [3] which is additional evidence that we have another instance of protective colloidal action, by which the crystallization forces of the metal are powerfully influenced.

Metallurgy. Since coarsely crystalline metals are brittle, tending to split along the lines of crystal cleavage, various physical and chemical means are employed in technical practice to obtain a hard, fine-grained structure.[4] Among the physical methods are chilling and rolling, while the chemical methods involve the removal of undesirable constituents (as in the conversion of pig iron into steel) or the addition of desirable constituents (as in case-hardening, and the manufacture of "chrome steel," "nickel steel," etc). For example, P. Putz has shown [5] that the predominant effect of vanadium in steel is to decrease the size of the

[1] J. Am. Electrochem. Soc., 1905, 8, 63.
[2] Z. Elektrochem., 1906, 12, 317; J.S.C.I., 1906, 484.
[3] Zsigmondy, J.S.C.I., 1902, 192; also Colloids and the Ultramicroscope, p. 81.
[4] P. Langmuir, Iron and Steel Inst., Sept., 1907; J.S.C.I., 1907, 1094.
[5] J.S.C.I., 1907, 614.

ferrite grains and make the material harder; it renders the ordinary structure due to pearlite fine-grained and homogeneous.[1]

Now, while the question is one of very great complexity, many of the facts at present available seem to indicate that one of the causes favoring the fine-grained structure is the inhibition of crystallization by substances colloidally dissolved in the molten mass. Thus, part of the carbon is iron and steel exists in the graphitic form, and as graphite is slightly soluble in iron [2] some of it will, under proper conditions, be found in colloidal form.[3] Besides metals may dissolve each other and other substances colloidally, but in the case of ordinary metals this is not easy to demonstrate.

An observation recently made by J. Alexander [4] is of interest here. Moissan [5] has noted that the addition of a little platinum to metallic mercury causes the latter to " emulsify " in water. Upon making up such an " emulsion " Alexander noticed that the supernatant fluid remained turbid upon standing, and therefore examined the fluid in the ultramicroscope, which revealed the presence of colloidal metallic particles in active motion.

Dyeing. The difference between a physical mixture and a chemical compound is frequently illustrated by dissolving out the sulphur from a *mixture* of iron filings and sulphur dust, and showing that the solvent, carbon bisulphide, does not affect the *compound*, ferrous sulphide. That in many cases dyeing is due, not to chemical combination, but to an adsorption [6] of the dye by the colloidal fiber, is evident from the fact that some dyestuffs can be extracted from the dyed fiber by means of alcohol. Investigation has shown that many dyes are colloidal in solution, and the selective coloring of various fibers, tissues, cells, nuclei, etc., is probably due to selective adsorption or the precipitation of one colloid by another. The ultramicroscope researches of N. Gaidukov [7] support this view.

The phenomena of dyeing are rather numerous and complicated, for the dyestuffs are numbered by thousands, and the various fibers, tissues, etc., such as cotton, silk, wool, linen, jute and straw, all react characteristically. In some cases the colloid fiber absorbs the dye, as with basic colors which dye silk and wool directly; in other cases there is necessary a mordant which is first absorbed and then fixes the color. Certain colors mutually precipitate each other and may in fact serve as mordants for each other, e.g., methylene blue and dianil blue 2R; patent blue V and magenta.

Colloid chemistry also throws much light upon many obscure points in the practical art of dyeing. It is possible to obtain much more level

[1] Beilby, Proc. Roy. Soc., A. 79, 463; J.S.C.I., 1907, 926.

[2] C. Benedicks, Metallurgie, 1908, 5, 41; J.S.C.I., 1908, 406.

[3] Carnegie Research Reports, J.S.C.I., 1908, 27, 570; F. Wust, J.S.C.I., 1909, 26, 412; Hersey, J.S.C.I., 27, 531.

[4] J.S.C.I., 1909, **28**, 280.

[5] Comptes rend., 144, 593; J.S.C.I., 1907, 413.

[6] In some cases adsorption may be followed by undoubted chemical combination.

[7] Zeitsch. f. angew. Chem., 21, 393.

colors in old dye liquors than in fresh ones, and here it seems that colloidally dissolved substances are responsible, exercising a restraining action upon the absorption of the color. The addition of Glauber's salt facilitates level dyeing, probably by its action as an electrolyte, producing a partial coagulation of the dyestuff, so that the particles of the latter, thereby made larger, are absorbed more slowly and evenly.

Soap. In a comprehensive paper entitled "Modern Views on the Constitution of Soap," [1] Lewkowitsch epitomizes the views of Merklen substantially as follows: "Commercial soap is a product having an essentially variable composition dependent upon (1) the nature of the fatty acids, (2) the composition of the 'nigre' (in the case of settled soaps), (3) the temperature at which the boiling is conducted; it behaves like a colloid and should not be regarded as a compound of sodium salts of fatty acids, with which a definite amount of water is combined chemically, but rather as an 'absorption-product' whose composition is a function of the environment in which the salts of the fatty acids happen to be at the moment of the finishing operation."

Merklen's views conflict with the views as to the chemical composition of soap previously advanced by Lewkowitsch, who states, in conclusion: "But whatever may be the outcome of renewed experiments, Merklen's views cannot fail to stimulate further research into the composition of soap, and thus help to raise the industry of soap-making, which has too long been looked upon as a mere art, to the rank of a scientifically well-founded industry, the operations of which are governed by the laws of mass action, the phase rule, and the modern chemistry of colloids."

The colloidal nature of soap solutions is indicated by their turbidity and their gelatinization. That the detergent action of soap is consequent upon its deflocculating effect was brought out in the interesting Cantor Lecture of H. Jackson,[2] who examined microscopically the supernatant fluid resulting from washing a dirty cloth with soap and water, and found in it countless particles in a state of oscillatory motion ("pedesis"). When an individual fiber was bathed in soap solution, the dirt particles gradually loosened and began to oscillate; upon substituting salt solution for the soap, the particles flocculated and the motion ceased. An ultramicroscopic examination of the detergent effects produced by soap should prove of interest. In this connection mention must be made of the excellent paper of W. D. Richardson on "Transparent Soap," [3] which he terms a supercooled or supersaturated solution, having distinctly crystalline tendencies, and exhibiting colloidal properties. Having in mind the fact that the salts of the higher fatty acids dissolve in water as colloids and in alcohol as crystalloids,[4] and also the fact that the alcohol or equivalent

[1] J.S.C.I., 1907, 26, 590.

[2] J. Soc. Arts, 55, 1101, et seq.

[3] J. Amer. Chem. Soc., 30, 414.

[4] S. Ya. Levites, Zeits. Chem. Ind. Kolloide, 2, 208 et seq., J.S.C.I., 1908, 1134; Mayer, Schaeffer, and Terroine, Comp. rend., 146, 484.

solvents (glycerol, sugar, etc.), are used in transparent soap, it seems probable that the crystals which frequently form in it are due to the slow separation of such part of the soap as is in crystalloid solution. This view is supported by the fact adduced by Richardson (loc. cit., p. 418) that the fatty acids separated from the crystals had a higher melting-point than those separated from the clear matrix. The isolation of the crystals was difficult because of their ramifying tendency, which recalls some of the crystal figures exhibited by some mixtures of crystalloids and colloids. What we may call the crystalloid phase of soap is apparently governed by the same factors as those which Tamman has pointed out as governing the crystallization of supercooled solutions, i.e., first, the specific power of crystallization; second, the speed of crystallization; third, the viscosity.[1] Thus, gold ruby glass when quickly cooled (or supercooled) is colorless, but acquires a red color upon reheating to the softening point. By ultramicroscopic examination Zsigmondy showed that the nuclei of metallic gold, which in the colorless glass were amicroscopic, grew into ultramicroscopic visibility in the red glass. It therefore seemed to the author that a most important factor in determining the transparency of transparent soap would be the speed of cooling, and some experiments were made along this line.

A piece of commercial transparent soap was melted and cast into two cups, one of which was quickly chilled in ice, while the other was allowed to cool slowly by immersion in hot water. The quickly cooled piece was transparent, while the other was practically opaque, and showed upon ultramicroscopic examination much larger ultramicrons than the transparent piece.

After standing three or four months, the quickly cooled soap was still transparent to the naked eye, whereas large opaque spots could be seen in the slowly cooled piece. In the ultramicroscope the former appeared as before, whereas the latter showed large and perfectly resolvable crystals in a clear matrix.

These experiments give us an inkling as to what occurs during the "heat treatment" and tempering of metals, and it is to be hoped that some technique may be devised that will give us even a clearer insight than does "etching," into the changes that occur in metals in metallurgy heat treatment, use, age, and even "disease" (tin for example).

Milk. From a colloid chemical standpoint, the main constituents of milk may be classified as follows:

In crystalloid dispersion	Salts (such as NaCl, etc.).
	Sugar (lactose).
In colloidal dispersion	Casein—an unstable or irreversible colloid.
	Lactalbumen—a stable or reversible colloid.

In suspension[2] milk fat.

[1] Zsigmondy, Colloids and the Ultramicroscope, p. 128 et seq.

[2] It is probable that some of the fat is in colloidal dispersion.

Most formulas and recipes for modifying cows' milk for infant feeding, and for that matter, many analyses, combine the percentages of lactalbumen and of casein under the collective title of "total proteids," thereby obscuring the highly important fact that the lactalbumen stabilizes and protects the casein from coagulation by acid and rennin.

The subjoined table will show how milks are influenced by a difference in the ratio between the casein and lactalbumen:

AVERAGE COMPOSITION

Kind of Milk.	Casein.	Lact-Albumen.	Fat.	Behavior with Acid.	Behavior with Rennin.
Cow....	3.02	0.53	3.64	Readily coagulates.	Readily coagulates.
Woman.	1.03	1.26	3.78	Not readily coagulated.	Not readily coagulated.
Ass.....	0.67	1.55	1.64		

It is interesting to note that the milks in the above table are arranged in order of their digestibility, which also corresponds with their relative colloidal protection. Thus Jacobi has stated that asses' milk has always been recognized as a refuge in digestive disorders in which neither mother's milk nor cow's milk nor mixtures were tolerated.

The addition of protective colloids to cows' milk stabilizes it and makes it act more like mother's milk when treated with acid and rennin. In fact, if sufficient protective colloid be added, coagulation of the casein in the stomach may be entirely prevented, or at least the coagula kept in a very fine state of subdivision.

The action of protective colloids is beautifully illustrated in the ultramicroscope, which enables us to see the individual particles of cows' casein in active motion and watch the course of their coagulation by acid, first into small and then into larger and larger groups, whose motion decreases as their size increases, until finally they sink out of solution in coagulated masses. If, however, some gelatin or gum arabic solution be added to the cows' milk before the addition of the acid, the casein particles continue their active dance and do not coagulate. In this connection it is interesting to note that the casein particles in mother's milk appear to be much smaller than those in cow's milk, probably because of the more highly protective medium in which they are formed and exist.

Although their method of action was not perfectly understood, protective colloidal substances have for years been used in the modification of cows' milk for infants. For over thirty years Jacobi has advocated the addition of gelatin and gum arabic to cows' milk and infant's diet, and the use of gruels, dextrinized starch and similar reversible colloids is familiar to all. It is interesting to note that sodium citrate, which is largely employed as an addition to cows' milk, acts as a protector, and when going into solution actually exhibits actively moving ultra-

microns in the ultramicroscope, a fact which indicates its colloidal condition.

In addition to stabilizing the casein, protective colloids in milk have a very important influence on the milk fat. In the first place it is to be considered the emulsifying and emulsostatic action of reversible colloids. Of much greater importance, however, is the result of stabilizing the casein, for insufficiently casein in curding carries down mechanically most of the milk fat present, yielding a greasy, fatty curd which is very difficult for the digestive juices to work on.

Ice Cream. It is a fact well known to practical ice-cream makers, and amply proven by experience, that ice cream made without eggs, gelatin, or some similar colloidal ingredient, is gritty, grainy, or sandy, or else soon becomes so upon standing; whereas ice cream made with small quantities of colloids possesses that rich, mellow, velvety texture so much in demand. Here the added colloid acts as an inhibitor of crystallization or practically speaking as a preserver of texture. The added colloid, especially gelatin, which is the one most frequently used, also serves as a protective colloid in preventing the coagulation of casein, an irreversible hydrosol, and a normal constituent of ice cream. In view of what has been said above, it is evident that gelatin thus renders ice cream more digestible.

A very misleading impression is given by some official food chemists referring to gelatin in ice cream as a " filler," which naturally leads to the idea that it is an inferior ingredient added in quantity to cheapen the product. But as gelatin is expensive and as but $\frac{1}{2}$ per cent is used, such a view is evidentally erroneous. The food value of gelatin as a protector of the body's nitrogen being generally admitted, and its effect in milk being very beneficial from a digestive point of view, its use in ice cream in the quantities referred to is necessary, legitimate, and scientific.

Confectionery. In gum drops, marshmallows, " moonshine " and other candies, use is made of gum arabic, gelatin, albumen, and other colloids to prevent the crystallization of the sugar. Thus, besides adding to the food value, they give the candy a smooth and agreeable taste, and preserve it in salable condition.

Brewing. Beer contains dextrin and albumin, both colloids. In the brewing process many factors appear which tend to coagulate the albumen. The influence of solid surfaces is illustrated by changing the walls of the fermenting vessel. Thus a certain wort fermented in glass or enameled vessels showed 0.2450 per cent of albumin; the same wort fermented in a paraffin lined vessel showed 0.1925, and in a vessel lined with pitch only 0.1750 per cent of albumin. Old-fashioned brewers would never use any vessel unless it had first been treated with a decoction of malt kernels and nut leaves, or else with " fassgelager " (barrel dregs) which acts like the so-called " bierstein," a deposit consisting chiefly of organic substances

that forms upon new surfaces and protects albumen from coagulation by their influences.

The influence of fluid surfaces is evident from the fact that in the chemical analysis of beer, benzine, benzol, chloroform, etc., may be used to coagulate and shake out the beer colloids.

The formation of gas bubbles tends to coagulate the dissolved albumen, and this fact killed the so-called " Vacuum Fermentation Process." The jarring due to transportation or even to passing trains may have a deleterious effect. A slight trace of acid tends to stabilize the albumen as do the tannin and resins from the hops, the dextrins from the mash and the inorganic colloids of calcium and magnesium. A proper balance between the dextrin and albumin is necessary for the formation of a lasting foam and a desirable " body " (Vollmündigkeit).

In America where beer is served icy cold, the chilling produces cloudiness, consequent upon a coagulation of albumen. This was cleverly overcome by Wallerstein, who introduced a proteolytic enzyme which increases the degree of dispersion of the albumen and thus prevents the clouding.

Tanning. The skins of animals (hide) constitute an organized colloid jelly, formed of bundles of fine fibrils, about 1μ in diameter, bound together by a cementing material of similar chemical composition, which is largely removed by the liming and other treatment, preceding the tannage proper.

When the swollen hide is placed in the acid tannin solution[1] (tan liquor), the tannin is powerfully adsorbed by the fiber and combines with it to form leather. It is still a moot question whether the combination is " physical " or " chemical," but since the fixation of the tannin follows an adsorption isotherm and is reversible in the presence of alkalies, it may justly be called a " colloid combination " which partakes of the nature of both. The positively charged hide and the negatively charged tannin mutually coagulate each other. Gelatin when neutral and free from electrolytes does not precipitate pure tannin, but in acid solution it takes a positive charge and is tanned. The tanning process may be aided electrically by giving the hide a suitable potential, positive in the case of tannin and negative in the case of chromium compounds.

Rubber. Rubber is made by coagulating the milky juice (latex) of various plants. Rubber lactices are emulsions stabilized by protective colloids (proteins or peptones) and the nature of the coagulant depends upon the nature of the protector. Thus, formaldehyde preserves latices whose protectors are proteins, but coagulates *Kickexia* latex by precipitating the protective peptones.

Vulcanization consists of the combination of sulphur with rubber. At first the sulphur is adsorbed; and then by heating, part of it enters into a close combination, probably true chemical combination.

Photography. The photographic plate owes its sentitiveness to an

[1] In alkaline solution both the tannin and the hide are negatively charged and no tanning occurs.

"emulsion" of colloidal silver halides stabilized by a protective colloid (gelatin, albumin or collodion). The degree of dispersion is controlled by the conditions of precipitation of the silver salt and the subsequent treatment of the emulsion (ripening). The latent image formed upon the exposure of the plate to light is probably an adsorption compound between colloidal silver and the silver halides.

Boiler Scale. In addition to containing various salts intended to precipitate scale-forming ingredients, most formulas for "boiler-compounds" and scale-preventing mixtures include such substances as glue, dextrin, starch, potatoes, tannin, extract of hemlock, etc. These colloids undoubtedly prevent the formation of hard crystalline scale, either by inhibiting to some extent the precipitation of the scale-forming salts or by keeping the precipitate in an extremely fine non-crystalline condition.

Cement, Mortar, and Plaster. When freshly mixed, cement and mortar contain colloidal sols or gels, which gradually coagulate or "set" and bind the crystalline elements of the plaster into a coherent whole.

The setting of plaster of Paris is delayed by glues, gums and other colloidal substances, and "retarders" of this character have been in use for years. On preparing some microscope slides with a mixture containing equal parts of plaster of Paris and water, to which has been added varying proportions of gelatin, the following results were observed:

Per Cent Gelatine.	Time to Set, in Minutes.	Microscopic Appearance of Slide.
0	40	Characteristic interlacing crystals of calcium sulphate.
1/100	50	No true crystals except in a few spots, where some colloid free solution had diffused out. Elsewhere aborted sphero-crystals.
1/10	260	No true crystals.
$\frac{1}{4}$	510	No true crystals.
$\frac{1}{2}$	960	No true crystals.
1	Not set in 48 hours.	No true crystals.
2	Not set in 48 hours.	No true crystals.

Filtration. Successful filtration depends upon the use of a septum or filtering medium, whose pores or orifices are small enough to hold back the particles it is desired to separate from the fluid; or the pores may become small enough by the deposit upon or in them of some of the precipitate, or of some added material, such as paper pulp or shredded asbestos. It is therefore evident that the presence of protective colloids, by tending to produce the finely dispersed or "hydrosol" condition of the particles, favors their passage through the filter. Thus a gold hydrosol with particles of 20–30$\mu\mu$ and containing albumen passed freely through a Pukall and a Maassen filter. In the absence of the protective albumen, the colloidal gold was adsorbed by the filter, gradually clogging the pores until

the filtrate, at first red, became colorless. In technical practice, wherever possible, a coagulated precipitate is formed, whose large particles are held back with comparative ease. It is very difficult to filter glue or gelatin solutions or precipitates formed in the presence of protective colloids.

The successful treatment of sewage, back-waters and trade effluents depends largely upon the separation from them of colloidal impurities by coagulation, adsorption and filtration. The old ABC method depended upon the use of alum, blood and clay (whence the name) to make a coagulum which would carry down suspended matter. Ferrous sulphate and lime (yielding a coagulum of ferric hydroxide), and alum are also used as clarifiers and coagulants. Filtration through sand, coke, etc., is made use of to adsorb dispersed impurities.

Animal charcoal and fuller's earth decolorize sugar and oils respectively, because of their powerful adsorptive action.

Chemical Analysis. The presence of colloids especially in technical products or solutions, may lead to grave errors in analysis, so that the chemist should destroy them by ignition, or else nullify their effects by the addition of a sufficient of excess coagulant or precipitant. Reversible colloids which are frequently referred to under the vague term "organic matter" may act: (1) By totally or partially preventing the formation of precipitates, just as tartaric acid and tartrates prevent the precipitation of alumina, chromic oxide, and ferric oxide;[1] (2) by preventing the satisfactory filtration of the precipitate formed;[2] (3) by rendering precipitates difficult to wash and purify.[3]

A few experiments will serve to make clear the importance of these remarks. Three solutions of lead acetate were taken; to the first was added hydrochloric acid which yielded a heavy coagulated precipitate; to the second was added sodium chloride (a less highly ionized precipitant), which yielded a colloidal precipitate of lead chloride; to the third was added first, a little glue solution and then sodium chloride, which in this case gave no visible precipitate at all.

Pharmacy. Colloids such as gum arabic, Irish moss, tragacanth, etc., are largely used in pharmacy in the preparations of emulsions. If ferric chloride be added to a gum arabic emulsion of cod liver oil, it coagulates the gum, and the oil, no longer protected by the emulsostatic action of the gum, promptly separates out.

Colloidal silver (collargol, argyrol), colloidal mercury (hyrgol, blue ointment), and colloidal sulphur (ichthyol), are largely used medicinally. Ferric salts, especially the chloride which readily hydrolyzes into the hydrate, act as styptics or hemostatics by coagulating the blood colloids. The action of disinfectants is largely controlled by colloid-chemical factors—

[1] Yoshimoto, J.S.C.I., 1908, 27, 952.
[2] Mooers and Hampton, J. Am. Chem. Soc., 30, 805.
[3] Duclaux, J.S.C.I., 1906, 25, 866.

the disinfectants are adsorbed by the bacteria and either coagulate their protoplasm or flock them out.

Foods and their Preparation. It is a serious error to judge foods upon the basis of a bald chemical or calorific analysis. Fat, protein, carbohydrate, and calories are not alone the criteria of food value—the physical condition of food largely governs its usefulness to the organism.[1] The experience of centuries has taught us the value of "light" bread or cake, leavened by yeast or baking powder until it presents an enormous surface to the digestive juices; unleavened bread was eaten only in time of stress, as we learn from the Bible. The meats yielded by young animals are more juicy and tender than those obtained from older animals, because the latter are formed from tissues partially dehydrated by age.

The ancient art of cooking involves many factors besides mere digestibility and assimilation; taste, flavor, odor and variety are important. Egg albumen when cooked is probably more slowly absorbed and loses its species-specificity; therefore some people who have an idiosyncrasy against raw eggs can eat cooked eggs. Cream is an emulsion of fat in an aqueous medium and *wets* paper; butter is an emulsion of water in a fatty medium and *greases* paper.

Physiology and Pathology. The changes which occur on almost all physiological processes are remarkable not only because of their very profound nature, but also because they are produced at comparatively low temperatures and in the presence of very dilute reagents. The living organism disintegrates proteins, oxidizes carbohydrates, and with the same apparent ease synthesizes substances of great complexity. Powerful reagents and high temperatures, which would be destructive to life, are necessary to bring about changes of this character under ordinary laboratory conditions.

The body and plant colloids (biocolloids) consist of carbohydrates (starch, cellulose, glycogen), proteins (plant and animal albumins), and lipoids (lecithin, cholesterin, fats and oils). Each tissue has a normal tumor or state of swelling, which is greatly influenced by acids, alkalies and salts. The *swelling and shrinking* of tissues together with their selective adsorption and the differential diffusion of solutions through them, account for or accompany many physiological phenomena, both normal and pathological. Thus, fibrin and gelatin swell much more in very dilute acid than in distilled water, but the swelling is depressed by salts. Fibrin is so sensitive that it swells in the presence of traces of acid quite undetectable by ordinary indicators such as litmus; in fact fibrin itself is a most sensitive indicator, and can by its swelling actually distinguish distilled water from the still purer conductivity water.

Local accumulation of acid in the organism may cause swelling (edema); for example insect stings, which may be imitated by stinging gelatin

[1] Previously neglected "impurities" are also of prime importance, i.e., so-called "vitamines" fat-soluble A and water-soluble B, etc.

with a needle dipped in acid. If acid accumulates in an organ with a rigid capsule (eye or kidney) the swelling tends to establish a vicious circle (glaucoma, nephritis) by compressing the blood vessels and cutting down the alkaline blood stream, which is unable to wash out the acids (mainly CO_2) formed by living protoplasm.

If the oxidation processes of the body are normal, the hydrogen in foods is oxidized mainly to water and the carbon mainly to carbonic acid—a gaseous acid which is exhaled without demanding protein or fixed alkali of the organism for its elimination. It would require nearly two pounds of pure caustic soda to neutralize the acidity produced daily by an average man. In the case of pathological oxidation, however, other acids are formed and a condition called "acidosis" may arise; which is in reality a diminished alkalinity, recognizable by the fact that an abnormally large quantity of bicarbonate of soda is needed to render the urine alkaline. These acids may cause disturbances of the body colloids, disease, and even death. In fact throughout life there is a gradual syneresis of the biocolloids, accompanied by visible shrinking and loss of water—compare the chubby hand of a child with that of an old man. In plants an analogous process occurs in lignification.

Digestion. The digestive process is preliminary to the actual adsorption and use of food by the organism, and has for its object the modification or change of the ingested food into such forms or such substances as may be absorbed in the lower part of the digestive tube. To have a correct understanding of the absorption of the products of digestion, we must bear in mind the fact that the walls of the digestive tract act as semipermeable colloid membranes and that absorption involves diffusion into or through these membranes or their constituent cells. Substances in crystalloidal solution, and colloidal sols whose particles are sufficiently small, represent then the two classes of digestion products which are diffusible and therefore absorbable.

Food as ingested consists mainly of substances that may be grouped into two classes:

1. Crystalloids—such as water, sugars, sodium chloride, etc.
2. Colloids—such as starch, proteins, emulsions, etc.

The crystalloids in foods are usually absorbed directly; although sucrose, for example, undergoes inversion. The colloids as a rule, are not directly absorbable and for the most part, digestion consists in the disintegration of the colloidal complexes of the food, so that they can actually diffuse into the organism and there undergo further changes. Colloidal gels or even sols whose particles are of large size, are practically speaking, nondiffusible, and must therefore be reduced to a more finely dispersed state.

Investigation has demonstrated that the high efficiency of the digestive juices is mainly due to small quantities of certain colloidal substances called enzymes (such as ptyalin, pepsin and pancreatin) which act as catalyzers, enormously hastening reactions which would otherwise proceed so

slowly that, practically speaking, they would not occur at all. The enzymes appear to act by forming with the substrate a combination of unstable character, which breaks down and liberates the enzyme again to continue the operation. Recently W. M. Bayliss, in his interesting monograph on "The Nature of Enzyme Action," has shown that in all probability "the compound of enzyme and substrate, generally regarded as preliminary to action, is in the nature of a colloidal adsorption compound." Anyone who has seen in the ultramicroscope the extremely active motion of the individual particles in colloidal solutions can readily imagine the terrific bombardment a substance must undergo when a colloid enzyme is concentrated on its surface by adsorption, and indeed it seems probable that enzymes actually produce their effects by virtue of their specific surface actions and the motion of their particles.

In order to find out if this idea could be verified by actual observation, the author watched under the ultramicroscope the action of diastase upon potato starch grains, and the action of pepsin upon coagulated egg albumen.

In the first case, actively moving ultramicrons in the diastase solution gradually accumulated about the starch grains, which after a time showed a ragged and gnawed margin. While the adsorption and motion of the larger ultramicrons was all that could be followed, the bright appearance of the field indicated that more numerous finer particles were present, and some apparently of intermediate size were seen.

For observations on albumen there was used a dilute solution of egg white which had been heated nearly to boiling. It was opalescent and in the ultra apparatus exhibited a field full of bright and rapidly moving ultramicrons. Upon allowing a droplet of essence of pepsin (Fairchild's containing 15 per cent of alcohol by weight) to diffuse in, an immediate coagulation occurred, the particles clumping into very large masses. A droplet of decinormal hydrochloric acid was then allowed to diffuse in, whereupon the large masses broke up in small groups and single ultramicrons, which once more resumed their original motion. Soon, however, the albumen particles began to grow smaller and disappear, the field all the while becoming brighter and brighter, indicating the concomitant appearance of smaller ultramicrons or amicrons. In vitro the addition of the pepsin to the opalescent albumen solution caused it to clear gradually, even at room temperature.

Enzymes are inactivated to a greater or less extent by shaking, heating, electrolytes, etc., all of which, as is well known, cause the coagulation of colloidal solutions and a resulting decrease in the activity of the motion of their constituent particles. Another feature of interest is that the action of enzymes is reversible, a fact that does not come much into evidence because of the dilution and removal by diffusion of the products formed. In cells, tissues and organs, however, changes of concentration again occur and synthetic processes may result.

One principle of colloid chemistry is of the utmost importance in digestion, namely, the protective action of reversible colloids, which stabilize or protect from coagulation, irreversible or unstable colloids. Mucin and analogous colloidal substances undoubtedly have a function of this character, which may in some cases account for the variance between the action of natural and artificial digestive juices. The effects of colloidal protection are in evidence in almost all physiological reactions and processes, and it is indeed extremely doubtful if there ever occurs in vivo any chemical reaction which is not greatly influenced by the colloids always present.

Absorption, Secretion, and Excretion. These are largely effected by the swelling and shrinking of the body colloids and by selective adsorption and differential diffusion. It must be remembered that the blood is in reality a circulating fluid colloid, whose attraction for water is greater in the " acid " or venous condition than it is in the " alkaline " or arterial condition. Tissues and organs well supplied with venous blood tend to absorb water (intestine); wherein those well supplied with arterial blood tend to give up (secrete or excrete) water (kidney); and as the blood is passing in a continuous stream, the process continues as long as the water supply permits and until the blood is in equilibrium with the other tissues.[1]

Conditions which decrease the capacity of the blood and tissues to hold water (diuretics, hyperglycemia and acidosis in diabetes) naturally result in the elimination of the excess or " free " water (polyuria, diarrhea).

Minute quantities of acid *increase* the swelling capacity of colloids, which quickly reaches a maximum, after which increasing acidity causes shrinking. Neutral salts oppose the action of acids apparently by driving back the ionization of the acid and thereby reducing the H-ion concentration which is the controlling factor.

The action of selective adsorption and differential diffusion in effecting secretion and excretion must be at once manifest. Easily hydrolyzable compounds may be this split up in the body, and yield secretions of acid nature like the gastric juice, or of alkaline nature like the pancreatic juice, depending upon the structure of the organ, the location of its cavity and of its afferent and efferent vessels, i.e., arteries and veins. Individual compounds in the blood stream or other body juices may also be selectively diffused out, concentrated, or separated from other accompanying substances. By selective adsorption, circulating substances may be fixed and taken from the circulation; in fact, poisons are usually taken up selectively by certain organs and tissues.

An insight into the mechanism of body processes may be obtained by

[1] The functioning of organs is largely controlled by nervous influences. Thus a sudden nervous shock may, by vaso-dilation, send an excessive supply of arterial blood through the mesenteric arteries (an " internal blush "), and result in secretion into the intestine (nervous diarrhea).

considering the functioning of the kidney. The Malpighian tufts are plentifully supplied with arterial blood having "free water," and under the pulsating pressure [1] of the blood stream, they ultra-filter off a very dilute but copious blood ultra-filtrate into the long convoluted tubules. The tubules, however, are plentifully supplied with venous blood, which is unsaturated with water and which therefore reabsorbs most of the water together with some of the dissolved substances contained in the preliminary excretion; so that there drips into the pelvis of the kidney a concentrated urine having in solution many of the substances found in the blood, but in a totally different concentration. Bechhold estimates that the average of two liters of urine voided daily by an average man, represents a preliminary excretion of fifty liters, of which forty-eight are reabsorbed within the kidney itself.

In plants, differential diffusion and selective adsorption seem to be intimately bound up with growth and the circulation of the sap. The plant tissues are mainly colloidal gels or finely integrated structures, and as the sap circulates or diffuses through them, each tissue selectively adsorbs and elaborates certain particular constituents. Thus with the potato and tapioca plants the starch-forming substances are fixed in the roots; with the sago palm they are fixed in the stem pith; and with cereal grains, in the seeds. As long as the adsorptive tissues are unsaturated or are multiplied, so long can growth continue, the stem and branches taking up the substances required for the upward growth, and the root taking up those required for the downward growth.

When we consider the great variety of biocolloids and their susceptibility to changes of structure and diffusive or adsorptive capacity, we can easily understand the almost infinite number of reactions that may go on within their recesses, as they swing the balance of the law of mass action over particles reduced to a reactive degree of subdivision.

[1] Since the vas deferens has a smaller lumen than the vas afferens, a "back pressure" is created within the Malpighian tufts.

CHAPTER LI

DEHYDRATED, DRIED AND EVAPORATED FOODS, CONDENSED FOODS

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The discovery that the removal of the water naturally present in food products would arrest the agencies of decomposition was made many ages ago. The ancient Indians and the savage tribes in Africa are known to have dried their surplus meat supplies, in order that they might not be in want when game was scarce or hunting difficult. Egyptian tradition called for the placing of dried food in the catacombs alongside of their dead, and it is said that dried kernels of grain, more than six-thousand years old when discovered in the catacombs in our time, upon planting, yielded perfect grain. These people made use of the sun's heat and the winds of the air to carry away the water in the food products, and, whereas the palatability and other properties of the dried material probably would not have appealed to the elaborate tastes of our present age, yet we cannot question their methods so far as the keeping qualities are concerned.

The North American Indian separated the fat of meat from the muscular tissue, drying the latter separately. When dried, or at least partially so, he melted the fat and mixed it with the dried meat which had been pounded into a paste or powder and, after adding a few service berries to improve the flavor, compressed the whole into cakes. This product is known to us as pemmican and is nowadays made of beef especially for the use of Arctic explorers.

In South America jerked or dried meat is known variously as *tassago* or *tassajo*, and jerked venison is prepared and used by mountain dwellers in the Rockies and our Southern Ranges. In South Africa these dried meat products are known as *biltong*.

Dehydration or Drying Compared with Other Methods of Preservation, Such as Cold Storage and Canning

Definitions. *Evaporated* food is generally understood to be the product resulting from the removal of only a part of the moisture naturally contained.

Condensed food has been concentrated to a higher degree than evaporated food, but still contains more water than dehydrated or dried food. It is usually semi-solid in condition.

Dehydrated or dried food has had practically all of its moisture removed, rarely containing as much as 5 per cent, and usually less than 2 per cent.

The process of drying gives a means of preserving food for storage possessing some great advantages over those of canning and of cold storage, while embodying practically every advantage obtained by the latter agencies

Dehydration greatly diminishes both the bulk and weight of the material, making it both easier and cheaper to store and transport. The food value is concentrated, while at the same time the preservation is secured by the removal of the water contained in the food, which out of every hundred pounds of fresh vegetables, fruits, milk, meat, and eggs is rarely less than 70, and in many cases more than 90 pounds. The following table shows the percentages of moisture in various foods:

TABLES SHOWING REMOVABLE WATER IN FOODS

Fresh Fruits

Percentage of water in edible portion:	
Apples	84.6
Apricots	85.0
Avocado	81.1
Bananas	75.3
Blackberries	86.3
Cactus fruit	79.2
Cherries	80.9
Cranberries	88.9
Currants	85.0
Currants (black)	79 0
Figs	79.1
Gooseberries	85.6
Grapes	77.4
Guava	82.9
Huckleberries	81.9
Lemons	89.3
Loquat	77.9
Mango	87.4
Medlar	74.6
Mulberry	84.7
Muskmelons	89.5
Nectarines	82.9
Olives	67.0
Oranges	86.9
Peaches	89.4
Pears	80 9
Persimmons (Jap.)	80.2
Persimmons	66.1
Pineapple	89.3
Plums	78.4
Pomegranates	76.8
Prunes	79.6
Raspberries	85.8
Raspberries (black)	84.1
Red bilberry	89.6
Rhubarb stalks	94.4
Roselle calyx	86.5
Roselle pod	84.0
Strawberries	90.4
Watermelon	91.9
Whortleberries	82.4

Fresh Vegetables

Percentage of water in edible portion:	
Artichoke	79.7
Asparagus	94.0
Beans, string	89.2
Beans, Lima	68.5
Beets	87.0
Cabbage	91.5
Carrots	88.2
Cauliflower	90.8
Celery	94.5
Chayote	82.0
Chickory root	79.2
Corn, sweet	75.4
Cucumbers	96.0
Egg plant	92.9
Leek	91.5
Lettuce	93.7
Mushrooms	88.1
Okra	87.4
Onions	87.0
Parsnips	83.0
Peas	74.6
Potatoes, Irish	75.0–80.0
Potatoes, sweet	69.0
Pumpkins	93.4
Radishes	91.8
Rhubarb	92.7
Spinach	92.3
Squash	88.1
Swiss chard	91.0
Tomatoes	94.3
Turnips	90.5

Other Foods

Beef	75.0–77.0
Hen's eggs	70.0
Milk	86.0–89.0
Fish	60.0–75.0

After removing the water the material in shrinking permits of close packing, and it may even be compressed into blocks or cubes. It can then be stored and shipped readily, not in expensive containers, heavy in themselves and containing additional weight of added water, but in light waterproof containers such as boxes lined with paraffined paper or made of paraffined fiber.

The shortage of glass and tin now prevailing will, therefore, not interfere with dehydrating, whereas it will handicap, more or less, canning and preserving.

The cost of handling and transporting equivalent amounts of canned and of dehydrated product of the same food material shows a saving of at least 80 per cent in favor of the dehydrated product.

At certain seasons farm products come in such great quantities that it becomes absolutely necessary to employ some ready means to prevent great wastage occurring every year. There are several factors which operate to produce wastage, among them irregularity of demand, inaccessibility of production, locality to canneries or refrigerating plants, and refusal of the consumer to purchase undersized material, which is perfectly sound and mature and equally as nutritious as the product of normal size and appearance.

During the year 1917, owing to the response to the President's appeal for greater production, which is estimated amounted to at least 33 per cent over and above normal, the amount of waste was greatly increased in spite of the fact that undoubtedly both canning plants and home conservation practiced were operated to an extent greater than ever before. Had this condition been foreseen a year or two earlier, we could have prepared to take care of all surplus material in dehydrating factories operating with less overhead expense than either the cannery or refrigerating plant.

As a food for armies in the field, dehydrated products are almost ideal. One of the most important features of the food conservation movement since the outbreak of the war has been the practice of dehydrating fruits and vegetables. During this food conservation campaign 246 new dehydration plants were erected, 190 of which were aided with Government funds. Since that time the number of plants has increased steadily, more than 2500 dehydrated food factories being in operation in January, 1918.

Development of the Industry. The processes for removing moisture on an industrial scale were resorted to primarily with a view of conserving material that would otherwise have gone to waste. The art was, therefore, largely developed by men who understood but little of its technical side. Furthermore, the product had to make its appeal to the consumer, largely, if not wholly, on the basis of cheapness. These two factors have combined to retard the higher development of the industry, as well as the improvement of the product.

In certain sections of the United States fruits are produced in such

large quantities that it becomes impossible to make use of them. Such states as Washington, Oregon and California, although blessed with a comparatively endless producing season, nevertheless face the difficulty of overcoming their great inaccessibility to the larger centers of consumption. There we find that the removal of moisture by evaporation is generally resorted to, and out of the experience of these fruit growers, improved processes of dehydration will be developed.

A fruit product from which about two-thirds of the natural contained moisture has been removed has found a place among our staple articles of food, and has become known to us under the name of *evaporated* fruit.

Evaporated fruit differs in flavor from the natural article. By improvements in the process a far superior article is now possible, very closely resembling the fresh fruit or vegetable. To distinguish the new product, the term *dehydrated* has met with fairly general acceptance.

Classification of Evaporators and Dehydrators. The types of evaporators which have been devised and patented are almost legion. The majority are intricate, and, granted that some of them will do the work for which they were devised, we find a large proportion of them too high in cost of operation. The types of driers which have survived, and which are operated with ordinary air under atmospheric pressure, can be grouped and defined about as follows:

1. *Drying Kilns or Drying Compartments.* These are composed of chambers of various forms and dimensions, and their principal distinction from other groups is that they are intermittent in operation. Generally in this type of drier the warm air currents pass across the material to be dried. They are often supplied with one or two lattice floors (for the kilns), and with trays, either fixed or in motion, for the compartment-driers.

2. *Tunnel or Progressive Driers.* In this class there are two general groups. In the one group we have those fitted with trays, which are conveyed either mechanically or by hand from the loading end toward the discharge end. In the other group we have the conveyor type of drier, also known as apron drier.

The principal distinction of this class consists in their being continuous, that is, the dried material passes through the entire drying chamber and is discharged at a point other than that of loading.

3. *Drum, Cylinder or Roller Driers.* This type of drier is rarely used for solid foods, with the possible exception in the case of production of potato meal. The driers of this class which are used for the concentration of foods consist of one or more cylinders, internally heated, and upon the outer surface of which the material to be dried is delivered.

Descriptions of Evaporators and Dehydrators. 1. *Drying Kilns or Drying Compartments.* Drying kilns are usually 20 by 20 feet square, and consist of a lower, or heating, compartment about 10 feet in height, and in which the heating apparatus, usually a large stove, is contained.

In order to provide better and more even heat for the air passing through, the stove flue is coiled about in the heating chamber before it is finally carried out to the top of the building. The top of this compartment has a lattice floor upon which the material to be dried is spread to a depth of from 2 to 6 inches, depending upon its consistency and the amount of moisture contained. During the process, which requires from eighteen to twenty-four hours, the material is turned over several times. The drying chamber proper is, at the center, about 12 feet high, sloping down toward the lattice floor to a point within a few feet thereof. At the top of the hood thus formed an adjustable ventilator is placed. In order to help the air circulation the gas flue from the heater is often lead up through this ventilator. Infrequently a second lattice floor is provided in this type of kiln. Most of the evaporated fruits now on the market, as well as hops used in brewing, are dried in this type of evaporator. In the second group of this class we have the kilns which are supplied with trays. These are either fixed in the kiln itself or are placed in racks on factory trucks which are wheeled into the drying chamber.

In the Hunter dry kiln, which is steam heated, air is taken in at the side, and in the space provided between the double walls, the air passes up around steam coils placed on this same side and continues through the double wall space at the top or ceiling and the opposite side. At the bottom of the opposite side air passes through the inner wall and into the kiln chamber. The air, before entering the kiln itself, in this manner has been used to warm the inner of the two sets of walls, which are the walls of the kiln chamber proper. The air passes out of the inner wall at the same side as it was previously admitted from the atmosphere, and, in flowing through the exhaust pipes, again passes the heating coils. This naturally increases the air circulation, but, on the other hand, uses up additional heat. The air flow is adjusted by means of dampers in the exhaust pipes, and the temperature, as well as the humidity of the air, are automatically controlled.

To humidify the air a water trough is placed where the air enters the kiln chamber. The steam coil running through the water in this trough is controlled by an automatic valve, which valve in turn is operated by the humidity controller. This whole arrangement belongs to the type of mechanisms called humidifiers.

The vegetables to be dried are placed on suitable trays, set in racks on factory trucks provided for the purpose.

Two other types of kilns worthy of mention are those represented by the Carson-Snyder evaporator and the "G. H." dehydrator. In the former, which employs natural draught, the trays are arranged in stacks, located zigzag fashion above the heating chamber. In each stack of trays the air openings are graduated in size, starting with a horizontal slot-opening of $1\frac{1}{2}$ inch in height into the upper tray. The openings are successively increased downward by an increment of $\frac{1}{2}$ inch, so that the

slot opening to the lowest member of the stack of twenty-two trays is $1\frac{11}{12}$ inches in width. It is apparent that the warm air in rushing upward will be prevented by the narrower openings from passing across the upper trays only, and in practice it has been found that excellent distribution of the circulation is obtained.

In the " G. H." dehydrator, illustrated in Fig. 374, the trays are suspended in an elongated compartment. In order to economize space the compartment has been extended up and down rather than horizontally, as will be plain from the illustration. The illustration shows a de-

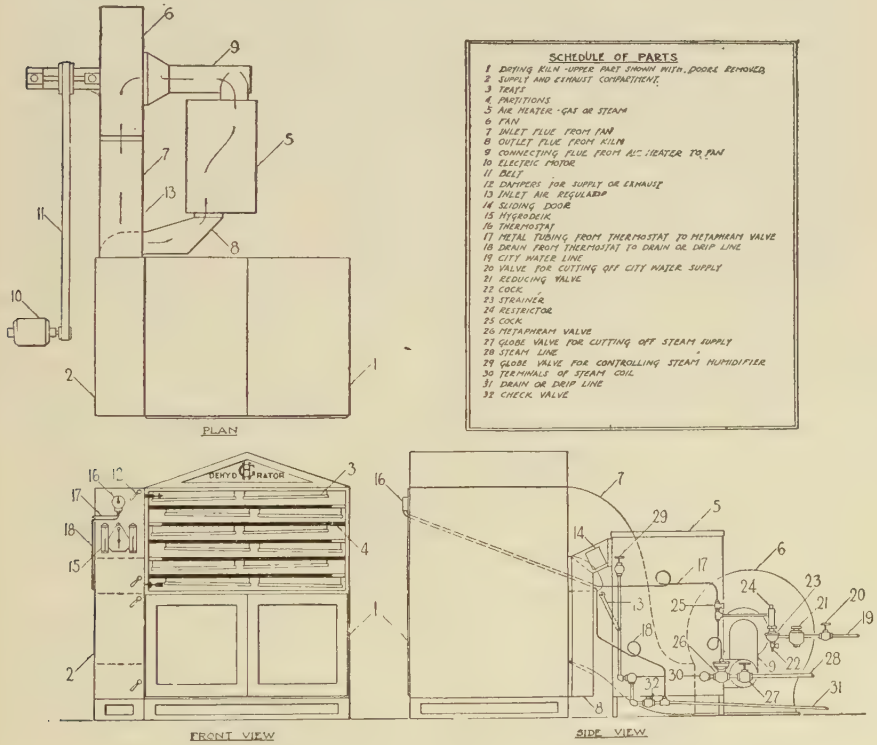
SCHEDULE OF PARTS
1 DRYING KILN -UPPER PART SHOWN WITH DOORS REMOVED
2 SUPPLY AND EXHAUST COMPARTMENT
3 TRAYS
4 PARTITIONS
5 AIR HEATER - GAS OR STEAM
6 FAN
7 INLET FLUE FROM FAN
8 OUTLET FLUE FROM KILN
9 CONNECTING FLUE FROM AIR HEATER TO FAN
10 ELECTRIC MOTOR
11 BELT
12 DAMPERS FOR SUPPLY OR EXHAUST
13 INLET AIR REGULATOR
14 SLIDING DOOR
15 HYGRODEIK
16 THERMOSTAT
17 METAL TUBING FROM THERMOSTAT TO METAPHREAM VALVE
18 DRAIN FROM THERMOSTAT TO DRAIN OR DRIP LINE
19 CITY WATER LINE
20 VALVE FOR CUTTING OFF CITY WATER SUPPLY
21 REDUCING VALVE
22 COCK
23 STRAINER
24 RESTRICTOR
25 COCK
26 METAPHREAM VALVE
27 GLOBE VALVE FOR CUTTING OFF STEAM SUPPLY
28 STEAM LINE
29 GLOBE VALVE FOR CONTROLLING STEAM HUMIDIFIER
30 TERMINALS OF STEAM COIL
31 DRAIN OR DRIP LINE
32 CHECK VALVE
PLAN
FRONT VIEW
SIDE VIEW

Fig. 374.

hydrator having two of these compartments and, as it is constructed on the unit principle, more may be added, if required. This dehydrator gives an excellent product, far superior to the ordinary evaporated fruit, both in flavor and appearance, and like the Hunter dry kiln, employs moist air. Humidifier and temperature regulator are also provided. This machine depends upon a fan blower, or an air pump for providing circulation, the regularity of the same insuring a uniform product. The trays in this dehydrator are made of wire cloth, like those employed in other driers for the same purpose.

2. *Tunnel or Progressive Driers.* The tunnel evaporator has been gradually perfected by modification of the Allen evaporator. It consists of a long, narrow room with floor and ceiling inclined uniformly from end to end, and with a furnace below the floor at the lower end. Extending parallel with the floor are cleats along which trays containing the material to be dried are moved from the upper end down to the lower end as the drying progresses. The heated air is admitted at the lower end of the tunnel from a furnace placed in the room beneath, and rising through the successive series of wire cloth trays, laden with moisture, passes off through a ventilator shaft at the opposite higher end.

Tray driers, whether tunnel, kiln, or compartment, can be used for a variety of foods; several kinds can be dried at one and the same time.

In the other group of driers in this class, the conveyor or apron type, it has been found less convenient to change adjustments than to dry one kind of material at the time. Conveyor driers are simple of construction and consist of cloth or gauze belts, discharging one onto the other and contained in a case or cabinet of suitable proportions. They can be designed to meet almost any requirement.

The improved Allen tunnel evaporator is used almost exclusively in drying prunes; and a form of wire cloth conveyor drier is used to produce dehydrated eggs.

3. *Drum, Cylinder or Roller Driers.* These driers are rarely used for fruits and vegetables. Abroad, potato meal is made by crushing boiled potatoes between rollers, all internally heated. Adhering to the hot cylinder surface they are dried and are removed by means of knives placed in contact with the cylinder surface.

Classification and Description of Vacuum Evaporators and Dehydrators. The driers operating under reduced pressure, or vacuum, come principally under three classes:

1. *Shelf Vacuum Driers* (see Chap. I). The food material, after suitable preparation, is spread uniformly over the internally heated shelves. Heat is also supplied to the hollow jacket surrounding the entire chamber. Steam or hot water is employed as the heating medium, depending upon whether high or low heat is required. This type of machine is used for drying non-liquid foods, such as vegetables and fruits.

2. *Drum Vacuum Driers* (see Chap. I). Consisting of one or two internally heated cylinders revolving in a vacuum chamber, these driers are used to reduce many food products, usually to dryness. The method of operation is easy to understand and control.

The food products usually dried in them are: Milk, eggs, fruit juices, meat and vegetable extracts, soups, potato meal, and coffee extracts.

A type of drum vacuum dryer having a fixed drum with rotary paddles is used to dry starch and other cereal products.

3. *Vacuum-pan Evaporators* (see Chap. I) are used exclusively for concentration of liquids to a pasty consistency. They are used as pre-

liminary concentrators for the rotary drum driers, these latter completing the drying.

Theory of Air Drying at Atmospheric Pressure. Dry and Moist Air. Moisture Capacity and its Measurements. Humidity and Temperature Control. There are two general processes of removing moisture by means of air, namely by natural and by artificial means.

The former involves the employment of the heat of the sun together with the winds of the air. The latter resolves itself into two subdivisions, to wit, drying with mechanically produced draft or with " natural " draft.

Sun and air drying at its best is unsatisfactory as a technical operation. Inclement weather and irregularity of atmospheric conditions, as well as the slowness of the process all combine to make it so. In addition the material is unduly exposed to insects and to contamination with micro-organisms and dirt. A preservative is nearly always needed to prevent decomposition because of the slowness of drying, and on account of the moisture retained after the drying has been completed. The term " air dry " signifies, as a rule, a moisture content of 10 to 12 per cent, and, without a preservative, micro-organisms and the enzymes naturally present will rapidly cause decomposition.

In dehydrating with mechanical draft, we need give but scant consideration to the feasibility of employing air at ordinary temperatures. The reason is plainly illustrated by the accompanying table showing the moisture carrying capacity of air at different temperatures. It will be seen that this capacity is doubled for every increase of 30° in temperature and that air at 160° F. (the average temperature of dehydrating) will absorb more than eleven times as much water vapor as air at ordinary temperature (70° F.).

The following table gives the vapor weights in grains which air is capable of absorbing to the point of maximum saturation, per cubic foot, for various temperatures at ordinary atmospheric pressure (29.921 inches of mercury).

Degrees, Fahrenheit.	Grains in a Cubic Foot.	Degrees, Fahrenheit.	Grains in a Cubic Foot.	Degrees, Fahrenheit.	Grains in a Cubic Foot.
10	1.1	80	10.95	160	90.5
20	1.56	90	14.85	170	112.7
30	2.09	100	19.95	180	139.4
32	2.13	110	26.4	190	171.0
40	2.87	120	34.4	200	208.3
50	4.11	130	44.5	210	252.1
60	5.79	140	56.9	212	261.7
70	8.02	150	72.0		

There are two general methods of securing the draft necessary in order that moisture-laden air may be displaced with fresh air. The one depends upon the principle that heated air will rise, and, if led into a tall

flue or chimney, will create a suction sufficient to draw in fresh air. The fresh air in this method is, of course, admitted below the material to be dried. In flowing upward it will absorb the moisture from its surfaces. This method usually does not permit the air to take up its full moisture capacity and is therefore wasteful of heat; nor does it permit of the advantages obtained from recirculating as does the other method, namely that employing fans or air pumps. The quantity of heat wasted by the former method is realized when we consider that the air is displaced in most rapid drying operations about six hundred times per hour. On the other hand the second process, while saving considerable heat, is charged up with the operation of a fan or an air pump. Where there is no available source of power, flue draft become necessary. Where moist (" humidified ") air is employed—and, to secure the best results, humidity is necessary—there is a further waste of heat, as the latent heat of vaporization of the contained water also becomes a factor. Here " recirculation " of the air, which provides for the use of practically its full moisture capacity, makes an additional saving, which is further augmented by the economy of humidifying with the moisture evaporated from the food itself.

Humidified air keeps the exposed surfaces of the food soft and permeable and thus permits of the easy escape of the internal moisture. Warm, dry air hardens the surface and retards the process. A much higher heat will be required to remove the moisture within, leaving a product inferior in both flavor and appearance, and often incompletely dehydrated. As the material becomes drier, the tendency for it to become scorched increases; dry air and this higher temperature are almost certain to produce a highly undesirable result.

To measure the moisture (humidity) contained in the air, the ordinary hygrometer is employed. The hygrometer usually consists of two thermometers, one with dry bulb exposed, and the other having its bulb coated with a film of water, by means of a wick dipping into water and delivering to a hood, usually of silk, fitted on to the bulb. The evaporation on the bulb lowers the reading of the latter and this rate of evaporation is dependent on the dryness of the air. The humidity is obtained from tables, in accordance with the dry and wet bulb readings. A " Hygrodeik," in addition to both thermometers, is supplied with a dial having affixed intersecting curves for dry and wet bulb readings respectively, by means of which the thermometer readings are interpreted into terms of humidity directly, without the use of tables.

There are several automatic humidity-controlling devices on the market, They can be employed on any system of drying where humid air is required.

Thermostatic temperature controllers are also obtainable and, to insure success, the temperature should be under control at all stages of the process.

Vacuum Drying Advantages and Practicability. Vacuum equipment is usually very costly and should therefore only be employed where the best air-drying methods fail. A very good product results, however, and in the case of substances which would be either decomposed chemically or have their physical state altered by subjection to the relatively higher temperatures needed in air drying, it is, of course, the only feasible method. The possibility of chemical change by exposure to the air is also avoided when removing moisture under vacuum.

The practice, as is quite generally understood, depends upon the principle that water will vaporize at decreased temperature when exposed to a vacuum, as shown by the following table:

BOILING-POINTS OF WATER AT DIFFERENT VACUA

Vacuum Millimeters of Mercury.	Vacuum Inches of Mercury.	Temperature, Centigrade.	Temperature, Fahrenheit.
756	29.74	0.0	32.
754	29.67	4.4	40.
751	29.56	10.	50.
747	29.40	15.6	60.
741	29.18	21.1	70.
734	29.89	26.7	80.
724	28.50	32.2	90.
712	28.00	37.8	100.
708	27.88	38.7	101.83
657	25.85	52.3	126.15
605	23.81	60.8	141.52
553	21.78	67.2	153.01
502	19.74	72.5	162.28
450	17.70	76.8	170.06
398	15.67	80.5	176.85
346	13.63	83.7	182.86
295	11.60	86.75	188.27
243	9.56	89.5	193.22
191	7.52	91.9	197.75
139	5.49	94.3	201.96
88	3.45	96.8	205.87
36	1.42	98.5	209.55
0	0.00	100.	212.

Consensus of opinion points to the conclusion that it is unnecessary to employ vacuum driers to dehydrate fruit and vegetables, as excellent results are obtainable by heated-air methods. This is in accord with the author's own experience.

Preparation of Fruits and Vegetables for Drying. As the cutting of the material greatly decreases the time of drying by providing larger drying surface, and as it is advisable, wherever convenient, to remove inedible parts, it has become customary to peel, core, or remove the pits and seeds from most fruits and vegetables before dehydrating.

The material after slicing, shredding, or crushing, is usually steamed or

"blanched" for one-half to fifteen minutes by exposure to live steam in a suitable chamber. This is necessary for many of the vegetables in order to prevent future activity of the enzymes present. The variation of time is dependent upon the consistency of the material. Two further objects are accomplished by blanching: the color is usually "set," and changes caused by the oxygen of the air; thus surface discoloration of

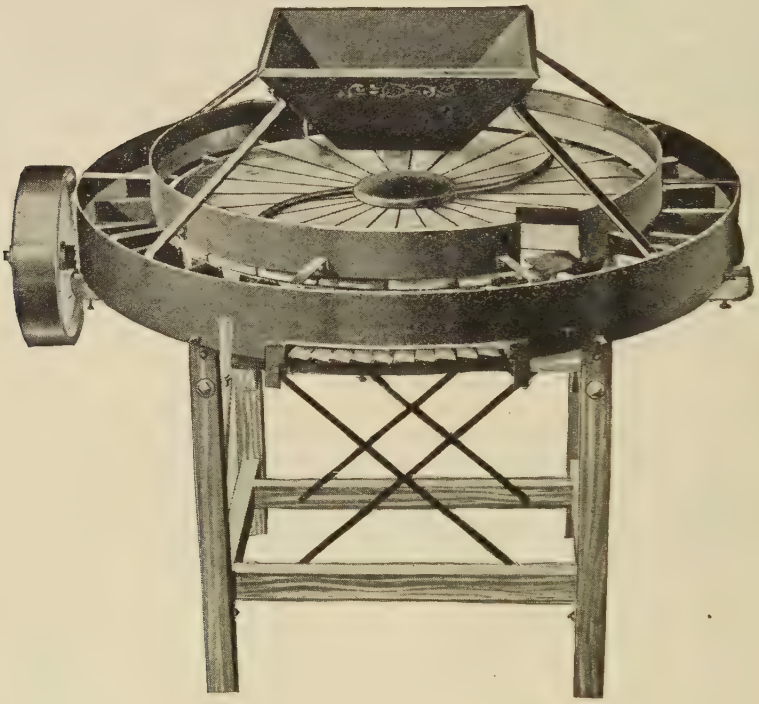

FIG. 375.—Slicing Machine.

apples and potatoes is prevented. "Sulphuring" is quite generally resorted to in the "evaporated" fruit industry. This is accomplished by conveying the material, usually after peeling, through a chamber in which sulphur is burned. This machine is called a "bleacher," and in it fruit is exposed to the fumes for about three-quarters of an hour.

With greens the sulphur is often burned directly in the kiln.

There is much doubt in regard to the unobjectionable qualities of sulphites in food and, until definite decision is arrived at, a quantity of 350 milligrams per kilogram of food has been tentatively suggested as an upper limit.

Some fruits, such as plums and grapes producing respectively, when dried, prunes and raisins, are dipped into boiling water or alkali in order

to crack the skins—baking soda (in proportion of 1 pound to 10 gallons of water) is least objectionable. The alkali should then be washed away. Mechanical perforation is sometimes employed.

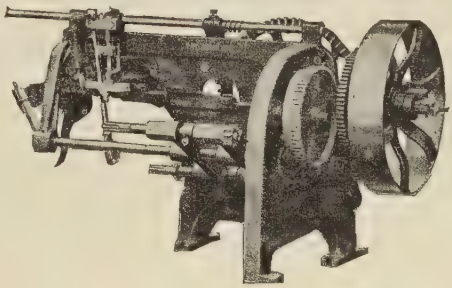

Fig. 376.—Automatic Parer and Corer.

Dipping the sliced fruit in weak solutions of salt, acetic acid, or citric acid, while serving to prevent discoloration during drying, is open to the objection that soluable nutrients are lost by this treatment. Peeling as well as cutting the fruit is done by machinery wherever possible. Knife or abrasive peelers (Fig. 376), and corers, large and small, are available as are also a variety of mechanical slicers (Fig. 375), and cutters. Better understanding of the chemistry of nutrition points to the desirability of leaving the skins on the products and merely subjecting the fruits and vegetables to thorough cleansing.

Technique of Drying. Temperatures Employed. Judging the Product and its Moisture Content. Packing, Reconstituting, or Rehydrating. The range of temperature employed in evaporating or dehydrating fruits is between 100 to 180° F. Some operators use the lower limit at the beginning of the process, gradually raising the temperature as the drying progresses. The time of dehydration varies from one to five hours in driers employing mechanical draft, whereas those depending on natural draft take from five to twenty-four hours, depending upon the product—the lower limits for greens and leaves, the higher for tubers and roots.

"Evaporated" products usually are incompletely dried and contain from 12 to 26 per cent by weight of water. Dehydrated products should be completely dried. They rarely contain over 2 to 3 per cent of moisture. The loss in moisture can be determined by weighing during the process; and reference to the table of normal moisture contents will aid in determining the progress at any time. The operator will soon become experienced enough to judge by the feel of the product.

In evaporating, the material should be removed from the drier when it still contains slightly more moisture than desired in the finished product. During the "curing" the surplus moisture evaporates. The curing process consists of piling the fruit coming from the drier, 1 or 2 feet in depth in a dark room or compartment at room temperature for from two to six weeks. This equalizes the moisture in the product, which is then ready for packing.

In dehydrating, the material is brought down to a lower moisture content and "conditioning" takes the place of "curing." "Conditioning" consists in keeping the material until any internally inclosed moisture

comes to the surface, which may be removed by a few minutes exposure in the drier. 48 hours will allow any internal moisture to come to the surface. When dehydrated vegetables or fruits are to be used, they are reconstituted by simply placing them in water, cool, tepid, or boiling, depending on the material, which is then ready for cooking. Reconstituting or rehydrating requires for different products from twenty minutes to six hours, and the material "comes back" with the bright natural color and goodly flavor.

Microscopic examination of dehydrated fruits and vegetables shows the cellular structure to be intact. As the material in dehydrating is never subjected to a temperature above 212° F., it is evident that the food value is not affected.

The evaporated product is packed in ordinary paper-lined wooden boxes, whereas the dehydrated product, being thoroughly dried and hygroscopic, requires moisture-proof containers.

Outline of the Plant (see Fig. 377). Inasmuch as the general routine is very similar in all fruit and vegetable evaporating plants, and, in a general way, is followed out in dehydrating plants, description of an apple evaporating factory will serve to illustrate the chain of operations.

(1) is the platform from which the apples are delivered into the storage bin (2), provided with a floor sloping toward the sliding door. The fruit as required is permitted to fall into the washing tank (3). From here a conveyor (4) delivers it into the grader, (5) where sorting takes place. Graders are fitted with cross screens of different meshes (or of bars set at various distances apart for vegetables like string beans) to separate the fruit or vegetables into different sizes as desired. The size to be put through first is delivered on to the conveyor (7) and the other sizes sorted into and set aside in containers (6). From the conveyor (7) the apples pass into the storage-bin, (8) which feeds the delivery tubes (9) leading to the peeling, coring, and trimming table (10). Three power-peelers and corers (11) are here shown, which discharge the peels and cores onto the conveyor (12) by means of which and the tube (13) they are transferred to containers in the basement. When peeled and cored the apples drop down on the inclined surface (to the right of the peelers in the illustration), and here the operator, after removing any imperfections with a knife, places the material on the conveyor, (14) which carries it into the bin (15) where it is picked up by the conveyor (16) and delivered into the "bleacher" (19). The bleacher is kept full of sulphur dioxide fumes by burning sulphur in the chamber (17), and the apples are slowly carried through to the tube (21), the sulphur vapors being drawn up and out through the pipe (20) by means of the draft in the flue (31) from the heater (32). From the tube (21) the bleached apples pass through the slicer (22) and are then either wheeled or conveyed into the drier (23). The type of drier here shown is the typical apple-evaporating kiln and similar to kilns used for drying hops. The sliced fruit is spread on the lattice floor. The moisture is carried

away by the hot-air currents. After being drawn in through the openings (29) and (30), around that part of the building, the air is then heated by passing the "hop-stove" (32) and around the flue coils (33) and passes out through the ventilator (28). The temperature of evaporation is controlled by adjustable dampers at (28). The fruit is spread in a layer 4 to 6 inches deep, and, after four or five hours, is stirred, more and more frequently as the drying progresses. When dry, the fruit is conveyed to the curing chamber (25) and then, by means of the tube (26) to the packing tables. The spaces on both sides of the hopper, indicated by (27), are used

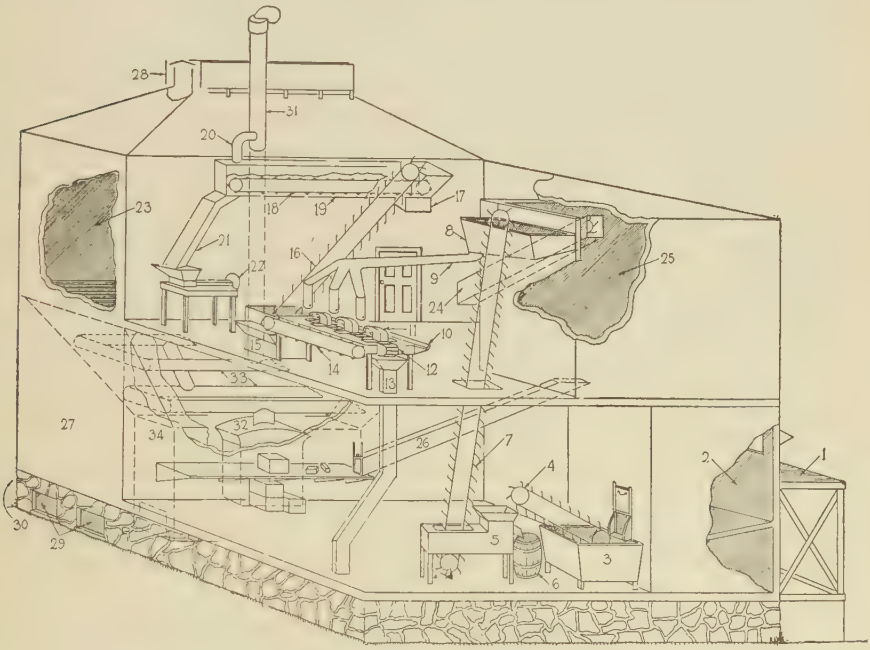

Fig. 377.

to store the boxes of finished product. The heater (32), indicated by the dotted outline, is a large hop-stove with a combustion chamber large enough to admit cord-wood. The hot flues (33) carrying the products of combustion into the air by means of the pipe (31) are first conducted up and around in the hopper-shaped, air-heating chamber (34), in order to increase the air-heating efficiency.

Scope of the Industry. The development of improved methods, resulting in the production of dehydrated fruits and vegetables, is of such recent origin that no data are as yet available.

The evaporated fruit industry being of longer standing furnishes some interesting figures, when we take into account the possibilities for improving this product.

In 1913, 1914, and 1915 there were exported from the United States

159,000,000 pounds, 88,000,000 pounds, and 128,000,000 pounds respectively of various evaporated fruits, not including raisins, which are produced in immense quantities. To illustrate, the quantity consumed in the United States in 1909 was over 200,000,000 pounds of evaporated fruits.

About 80 per cent of all the evaporated fruit comes from California, where enormous quantities of hops are also dried.

Condensed and Evaporated Milk. Milk Powder. The following definitions apply to these products:

Condensed Milk. This term is invariably applied to milk partially dehydrated and preserved with cane sugar. It is made from whole milk or from partially or wholly skimmed milk according to requirements. Condensed whole milk is composed of about 32 per cent of milk solids and 41 per cent of added cane sugar, the balance, 17 per cent, being water.

Condensed skimmed milk is of about the same consistency but contains not more than 1 per cent of butter fat. Plain condensed milk, in trade circles, is understood to apply to milk that is concentrated and sold in bulk without the addition of cane sugar. Plain condensed milk actually is evaporated milk brought down to a higher degree of concentration.

Evaporated Milk. This is normal milk which has been reduced to one-half of its original bulk. It contains about 25 per cent of milk solids. This product was formerly labeled " evaporated cream," but the Pure Food Laws prohibiting misbranding stopped this misleading practice.

Whole Milk Powder. This is the entire milk which has had practically all of its moisture removed. It consists of about 97 to 98 per cent milk solids, the remaining 2 or 3 per cent being moisture.

Whole Skimmed Milk Powder. This is made by concentrating skimmed milk down to the solid state. It contains between 3 and 5 per cent of moisture.

Like vegetables and fruits, the nutritional principles of milk are greatly diluted with water, which, while necessary from a physiological standpoint, yet makes the food expensive to transport and to store. There is about 88 per cent of water in normal milk, which, in addition to its weight, also is objectionable in that it renders the fluid especially susceptible to contamination.

The dehydration of cow's milk, partial or complete, produces, in the former case, the condensed and evaporated milks so familiar to us all. In the latter, the dried milk is either sold as milk powder, or, when mixed with powdered malt principles, as malted milk.

The removal of moisture from cow's milk dates back to the year 1800. In 1856, an American, Gail Borden, succeeded in manufacturing condensed milk on a large scale in his factory at Wolcottville, Conn. Five years later this new industry received great stimulus through the demand for concentrated foods created by the Civil War.

The condensing processes have gradually been perfected to such an

extent that it is even possible to remove practically all the water of the fluid milk, leaving a dry powder of excellent keeping qualities and taste. When redissolved in water this product is practically similar to that of fresh pasteurized milk. The reduction in bulk, as effected in the various concentrated milks, ranges between one-half and seven-eighths of the original volume.

To produce a good quality of condensed milk the fresh fluid naturally must be of superior quality. It is necessary that the milk condensery should control and supervise production; sanitary conditions on the dairy farms should be insisted upon, and milk should be handled with the greatest care. No feed which will impart its flavor to the milk should be given to the cows, as the flavor will be developed and intensified by the concentration. Bacteriological examinations should be made regularly, and, as the milk is purchased on the fat percentage basis, all deliveries of milk must be tested. An acidity of over $\frac{2}{10}$ of 1 per cent of lactic acid may prove objectionable. The milk, after weighing, is poured through a large strainer, from which it runs directly into large enameled vats, equipped with stirrers. This room is kept as cool as possible.

An indifferent quality of condensed milk may be made by forcing hot air through the milk kept at 140° F. In this process the cream is usually separated before concentrating, and, after concentration of the skimmed milk is complete, the two are again mixed with the aid of a homogenizer, subsequent to pasteurization.

Milk is usually condensed in vacuum pans, either single or double effect. The latter is the more economical, the second pan being heated by the water vapors from the milk in the first pan. The milk is run from the storage tanks into the hot wells where it is brought to a temperature of about 150° F. It is then delivered into vacuum-pan evaporators, where the evaporation is continued at a temperature of 175°. When a consistency indicated by Baumé readings of 10° and 14° respectively for whole and skimmed milk, have been reached, the milk is superheated by blowing steam through it in the vacuum pan until it thickens. When sufficiently thick the steam is shut off and water is admitted into the condenser to obtain the proper consistency. The product is then subjected to a vacuum of about 26 inches gradually. The vacuum is released and the milk drawn into 10-gallon cans and by means of a cooling tank brought down to 36° F.; finally the cold water in the coils of the cooling tank is displaced with brine or ammonia. This manipulation is said to overcome precipitation or crystallization in the finished product.

Sweetened condensed milk, made from whole milk, is condensed in the proportion of four to one, and the sugar added is about 1 pound to each 3 quarts of milk condensed. The sugar is either dissolved separately in a small quantity of hot milk or hot water and gradually added to the milk in the vacuum pan, or it may be dissolved in a small amount of warm fluid milk and run into the product after condensing.

Partly skimmed milk, or all skimmed condensed milk, receives 1 pound of sugar for each four quarts of skimmed milk to be condensed. It is used principally by bakers and confectioners.

Evaporated milk is condensed in the vacuum pan until the desired consistency is obtained; it is then quickly cooled to about 60° F. and put into cans and sealed. The cans are placed in sterilizers where they are heated to about 240° F., during constant agitation, for eighteen to forty-five minutes, depending principally upon the size of the can. After sterilization the cans are immediately cooled and placed in a shaking machine where agitation is continued until the product is perfectly smooth.

For the manufacture of condensed milk the equipment required consists of a boiler, engine, scales and weighing can, receiving vats, milk heater, hot wells, vacuum pan and condenser, vacuum pump, cooling tank, and cans.

In condensing skimmed milk there are required, in addition to the above, a separator, vats, pasteurizers, and coolers for handling the cream.

Manufacturers of sweetened condensed milk, on the other hand, could get along with the same equipment as is used in a plant making plain condensed milk, or, in the event of adding sugar before condensing, a separate tank in which to dissolve it would be needed. If the products are to be canned, machines for filling and sealing cans would be needed; where cans are not purchased from outside can manufacturers, machines for making them would also be necessary. Evaporated milk manufacture requires a tubular cooler in place of the cooling tank; also a sterilizer, and a shaking machine.

Scope of the Industry. In 1910 there were over 300 milk-condensing plants in the United States located in twenty-four different States. These plants had a capacity of over 15,000,000 pounds of milk daily, and represented an investment of more than $15,000,000 in buildings and equipment alone.

Dehydrated Milk or Milk Powder. This product is of comparatively recent introduction and has only of very late years been brought to that high state of perfection where the original properties and complete solubility are retained. The first descriptions of dehydration processes for milk were published about 1900.

Due to the difficulty of preventing the fat from becoming rancid, until very recently, the entire amount of milk powder manufactured was made from skimmed milk. About 9 pounds of dehydrated skimmed milk powder is obtained from 100 pounds of whole milk. $3\frac{1}{2}$ pounds of butter fat are also obtained at the same time.

Like most dehydrated products milk powder is hygroscopic and must therefore be packed moisture-proof and kept in a dry, cool place.

Dehydrated milk possesses all the valuable properties of fresh, sweet milk, and it can be used in the dry form by bakers and confectioners or it may be brought back to its original liquid state by adding an amount

of water that has been extracted from it. There are two general methods of producing dehydrated milk. One method, less frequently employed, consists in spraying the milk into a hot-air chamber. The solid particles striking against a screen separate the dry powder from the moisture-laden air. A second method, more generally used, consists in spreading the milk on a revolving, internally heated cylinder, the adhering film, drying in a little less than one revolution of the cylinder, is scraped off in sheets. Before it is delivered to the cylinder dryer, the milk is usually partly condensed in vacuum pans.

The following brief descriptions will illustrate the modifications of the above methods as used in several successful systems:

In the *Passburg System* the cold milk is fed on to a large iron cylinder, internally heated, and revolving in a vacuum chamber. After completion of nearly one revolution, the milk has been completely dried and is scraped off in sheets. This product is then ground and bolted in exactly the same manner as employed in grinding flour from cereals.

The *Ekenberg System* provides for the separation of the fat from the milk. This cream is promptly pasteurized and cooled. Where it is desired to prepare whole milk powder, the cream is kept in insulated vats at a low temperature secured by brine coils, and is reunited with the dehydrated skimmed milk powder.

The skimmed milk powder is produced by allowing the fluid milk, to flow into so-called exsiccators. Briefly, these are large vacuum chambers in which a very large revolving cylinder is contained. The products chamber, connected with the vacuum chamber, is provided with a series of gates so as to allow the removal of the dehydrated milk. This products chamber together with a milk chamber (also attached to the vacuum chamber), as well as a condenser to remove the evaporated moisture, are all kept under a constant vacuum. The milk is spread upon the revolving cylinder and is dehydrated at a temperature rarely exceeding 110° F. and under a very high vacuum. After being scraped from the cylinder the dried film of milk is delivered to the products chamber, from which it is removed and placed in a heated compartment. Here the last traces of moisture are removed at a temperature of 90° F. It is then ground into a very fine powder by means of water-cooled mills. This process produces a superior quality of dehydrated milk.

Another *vacuum process* is carried out as follows: The fluid milk, after removal of the cream, is evaporated in vacuum pan evaporators to a consistency of about 40 per cent of total milk solids and at a temperature between 135 and 138° F. Single- or double-effect evaporators are employed, the latter being more economical in operation. The milk is then held in storage tanks from which it is fed into vacuum cylinder dryers, where it is dried on revolving cylinders internally heated by steam, the temperature not exceeding 138° F. By a special mechanical device the milk is spread in a thin film or to the surface of the heated cylinder

surrounded by a vacuum of 28 inches or more. The milk is dried during one revolution and is scraped off in the form of flakes, which are then ground and bolted. The milk produced by this process is said to be so soluble that it will dissolve perfectly even in ice water.

The *Stauf System*, devised by Robert Stauf of Posen, Germany, is typical of several of its kind now employed commercially in the United States, and consists in atomizing the milk in regulated currents of hot air. The amount of air and heat is so adjusted as to completely absorb the moisture of the fluid milk, and the resulting dehydrated product is separated from the moisture laden air by means of a screen. This product does not require grinding. Where systems of this kind are employed it is frequently customary to reduce the milk in vacuum pans to about one-fifth of its volume.

In the *Just System*, milk is spread on the surface of two inversely revolving cylinders, heated internally with steam at a pressure of about 45 pounds to the square inch. The film of milk is very thin, and at this temperature, considerably above the boiling-point of water, the milk is quickly evaporated. The cylinders revolve with a speed of about six revolutions per minute and are surrounded by a current of air, produced by a fan exhauster placed in the exhaust flues. The dehydrated milk is scraped from the cylinders by knives held in contact with the surface. The flakes are ground, and, after cooling, are ready for packing.

The *Campbell System* depends for its results upon the principle of forcing warm, sterilized air up through the milk to be condensed. These concentrators are usually rectangular in shape and are equipped with coils in the interior, as well as a circulating medium of hot water surrounding their exterior. The escaping air thoroughly agitates the milk, imparting to it a rolling motion producing fairly rapid evaporation. As the concentration increases, the temperature is decreased. When the product has been reduced to a pasty consistency, the opening of a gate valve allows the mass to fall into large roller drums located on the floor below. These drums are usually tin plated and have cone-shaped ends. The revolving drum carries the mass up to the top from whence it drops down to the bottom. A blast of heated air passing through the drum vaporizes and carries off the moisture in the dropping particles. As the paste becomes drier, its weight causes it to move and twist unequally, thus breaking it up into smaller particles. These are then conveyed to the dryer drums where the dehydration is completed. These dryer drums are equipped with a central shaft and lateral arms extending down into the mass. Sterilized air is forced through the shaft and arms and a constant rolling of the drum completely exposes the material to the hot air currents. When thoroughly dry, the lumps are conveyed to a grinder, where they are reduced to a coarse powder.

Scope of the Dehydrated Milk Industry. In 1910 there were approximately 8,500,000 pounds of dehydrated milk produced by ten factories

in the United States, located in five States, namely, Vermont, New Jersey, New York, Michigan, and California. Indications are, owing to the demand for dried milk created by the steady increase in the price of the fluid-milk supply in our larger cities (as well as war needs), that by 1920 the output of dehydrated milk plants will have at least more than quadrupled. The process of dehydration, when worked on a large scale, is inexpensive, and the ease with which the product can be handled and stored as well as shipped, will many times offset the cost of the process and provide for the city dweller a reasonably priced and highly nutritious food.

Dehydrated Eggs or Egg Powder. In accordance with the use to which the product is to be put, eggs are either dried whole or the yolks and whites are dried separately. Dehydrated whites of eggs are known in the trade as egg albumen, and the yolks as dried egg yolk. The whole dried egg is known as egg powder. A simple method of drying eggs, but having many objectionable features, consists in spreading the thoroughly agitated liquid egg mass in a thin layer on a copper cloth belt. This conveyor belt is usually enclosed in a drying chamber through which warm air currents are discharged from a fan blower. At the best this process is not very rapid and the product obtained is not very good.

A superior product, possessing excellent powers of solubility, is obtainable by employing vacuum drum dryers similar to those employed in dehydrating milk. After being broken up, the egg mass is thoroughly agitated and then spread upon the surface of the revolving drum. As the temperature of evaporation must be kept very low in order to prevent the coagulation of the egg proteins, a high vacuum is applied. The temperature employed is about 110° F., hot water being used as a heating medium. The film of dehydrated egg upon being scraped off is then reduced either to the size of rice grains (" riced "), or to a powder more or less fine.

Dehydrated Vegetable Extracts. Plant extracts, such as those of coffee and of vegetables, particularly soup vegetables, as well as meat extracts, are invariably reduced to dryness by means of drum or cylinder vacuum evaporators. Familiar staples on the market are soluble coffees, bouillon cubes, soup cubes, with or without dehydrated vegetables, beef extract and the like. So-called bouillon cubes have been found on the market principally composed of common salt to an extent of about 75 per cent of their weight. In fact, from a standpoint of nutrition, a bouillon cube which contains none of the fat from the meat possesses practically no nourishment whatever. The meat extractives are merely stimulating physiologically, but can be made nourishing by combination with vegetable extractives.

Dried Fish. This is a product comparable to evaporated fruit or milk, but having had only about one-half of its original moisture removed. The process of drying fish is known as " curing " and is effected by spreading the fish on so-called flakes. The flake consists of a lattice

bed about 8 feet wide and 30 inches high, and of a length to suit requirements. The lattice used on this bed is made of triangular strips 1 inch on the base, and these are placed about 3 inches apart. The fish, therefore, rest upon the sharp edge about every 4 inches. This is for the purpose of giving a maximum circulation of air about the fish. A second shelf or " deck " is often provided, the space between decks being about 18 inches.

After dressing and removing the bones and skin, the first stage of the drying is effected by " pickling " with salt. The fish are carefully placed in large hogsheads with the face (split surface) side up, excepting the last two or three layers. Each layer is completely covered with salt and the piling is usually continued about 8 inches above the level of the butt or hogshead to allow for settling. By this arrangement the moisture is drawn out of the fish, and, together with the salt, forms a pickling fluid in which the fish are left until convenient to spread on the flakes for the second and final stage of the drying.

The loss in weight from salting is about 40 per cent of the dressed weight or 17 per cent of the live weight. The fish will keep indefinitely in the strong brine of the pickle so long as they are completely covered. As there is slight leakage, pickle must be added occasionally to make up for this loss. This part of the process requires about ten days for its completion.

The fish are then taken out and stacked in a kench to drain off part of the brine. As soon as favorable weather obtains and the pickle brine has drained off fairly well, the fish are transferred to the drying flakes as described above. If the sun is fairly warm and there is a good breeze, the process can be accomplished in about twelve hours. To " hard dry " the fish it is necessary to remove it from the flakes and pile it in a kench to be " sweated." The salt crystallized on the surface of the fish while exposed on the flakes draws out the moisture from the interior, so that the second drying on the flakes has a greater effect. This is a comparatively crude process of drying and in the light of recent knowledge there is a great deal of room for improvement.

Utilization of Waste from Dehydrating and Evaporating Plants. Rabak has shown that oils can be obtained from kernels and seeds of various fruits.

Cores and peelings from various fruits can be used in vinegar manufacture. For each ton of these trimmings there will be obtained, on pressing, about 135 gallons of juice for such purpose. The pomace, after pressing, makes a good cattle feed, or it can be used to manufacture concentrated pectin. Pectin is a jelly making principle present in fruits and vegetables, and the concentrated article is used in jelly factories. The egg shells obtained from egg-powder factories, when crushed, can be used as a source of lime necessary in the diet of egg-laying hens.

The trimmings obtained when drying fish make an excellent fertilizing material.

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CHAPTER LII

BAKING

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Definition. Baking as generally understood is the *art* and *industry* of preparing appetizing and healthful food products, using crushed or finely ground cereals as the principal materials, subjecting the same, suitably prepared, to baking in a hot oven.

Products. To-day many are the products resulting from baking, a few names of which are given in the following list:

Bread. (Water bread, milk bread, whole wheat bread, bran bread, rye bread, pumpernickel bread, Swedish knake bread, Boston brown bread, New England brown bread, potato bread, Indian corn bread.)

Rolls. (Parker House rolls, French rolls, Swedish rolls, Vienna rolls, sweet rolls, fruit rolls.)

Rusks. (Zwiebach, French rusks.)

Coffee Cake. (Tea rings, apple cake.)

Buns. (Hot cross buns.)

Muffins. (Grilled muffins, hominy muffins, rice muffins, oatmeal muffins, imperial muffins.)

Biscuits. (Baking powder biscuits, soda biscuits scones, tea biscuits, fruit biscuits, rye gems, cornmeal gems.)

Cookies. (Gingerbread, sour-milk gingerbread molasses gingerbread ginger snaps, molasses bars, spice cookies.)

Cake. (Sponge cake, sunshine cake, moonshine cake, lady fingers, jelly rolls, egg cake, walnut cake, cup cake, cinnamon cake, devil food cake, banana cake, golden corn cake, angel food cake, marble cake, gold cake, silver cake.)

Wafers. (Scotch wafers, vanilla wafers, almond wafers, rolled wafers, cocoanut wafers, chocolate wafers, Nurembergs, Swedish wafers.)

Pies. (Cream pies, cocoanut pies, chocolate pies, apple pies, peach pies.)

Flour-production note. The American people consume 8,600,000,000 lbs. of wheat flour and 1,000,000,000 lbs. of rye flour, all of which is made into the baked products. 1,000,000,000 lbs. of wheat flour is made into fried cakes, waffles and griddle cakes and used for thickening gravies. A very small amount of inferior flour is used for foundry purposes and some flour is used in the preparation of special medicinal foods, starches, etc.

Consumption. The American people are now annually consuming nearly 10,000,000,000 lbs. of baked products, of which 5,700,000,000 lbs. is wheat bread; 1,000,000,000 lbs. rye bread; 900,000,000 lbs. soda biscuits; 350,000,000 lbs. sponge cake; 420,000,000 lbs. rolls; while all the other baked products consumed approximate 1,720,000,000 lbs. Wheat bread is the main baked product, equaling 57 per cent of the total weight of all products consumed. Rye bread represents 10 per cent of the total baked products consumed; while 84 per cent of the total flour used in baking is wheat flour, the balance being rye flour, corn flour, barley flour, oats flour, rice flour, and potato flour.

Handicraft. (Home baking.) Considerable baking is done by the housewife in her home kitchen. Nearly one-half of the baked products consumed are made there; especially is this true in the rural districts. Almost every variety of baked products are made in the home (bread, rolls, rusks, coffee cake, muffins, biscuits, cookies and cakes).

Kitchen equipment consists of either a coal, wood or gas stove, with oven attachment, pans, bowls, and spoons. Materials of all kinds are employed, such as wheat flour, rye flour, special flours, sugar, salt, flavoring extracts, various kinds of yeast, eggs, nuts, milk, baking powder.

Method. The housewife generally bakes according to her own judgment based upon experience or by following directions in a cook book or advertising literature. Following are a few recipes showing proportion of materials used and description of method employed to obtain the various baked products in an ordinary home kitchen:

Wheat Bread.

8 cups flour	3 tablespoons sugar
3 cups water	3 teaspoons salt
1½ tablespoons butter	½ yeast cake dissolved
2 tablespoons lard	½ cup water

Place sugar, salt, butter and lard, in a bowl and add the water. Warm to such a heat that it will be lukewarm when mixed. Then add yeast previously dissolved. Then mix in flour and knead into a dough. Place bowl in a warm place and cover with a cloth. Allow to rise over night, cut down with a knife, allow to rise for one or two hours longer. Shape into loaves, place in pans and allow to rise in a warm place. When dough has about doubled in volume then bake in a hot oven.

Parker House Rolls.

4 cups flour	1½ teaspoons of salt
½ cup milk	¾ yeast cake dissolved
1½ tablespoons sugar	½ cup water

Mix ingredients as for bread dough, allow to rise to top of bowl. Cut down and allow to rise again, cut down and knead dough on board. Roll

out and cut with biscuit cutter and shape into biscuits. Make crease in center of each piece with knife previously dipped in flour.

Sponge Cake.

2 cups flour	¼ teaspoon lemon extract
4 yolks of eggs	2 whites eggs
2 cups of sugar	½ teaspoon salt
½ cup milk	3 teaspoons baking powder

Beat yolks thoroughly and add the sugar and continue to beat. Then add water, lemon extract, whites of eggs beaten stiff, then stir in flour previously mixed with baking powder and salt. Bake fifteen to twenty minutes in a moderate oven in a buttered pan.

Baking Industry. About one-half of the baked products consumed are made in bake shops or factories and sold to the people for profit. The number of such establishments in America at present is 29,324, representing invested capital of $1,100,000,000. There are 230,000 persons engaged in the industry, of which 36,000 are proprietors and firm members, 4000 salaried officials, superintendents and managers, with 30,000 male clerks, 150,000 wage earners. $10,000,000 is annually paid to officials; $20,000,000 is annually paid to clerks; $115,000,000 is annually paid to wage earners; $14,000,000 rent for factory space; with $4,500,000 paid to taxes and internal revenue and corporation income; with $350,000,000 annually for principal materials; $20,000,000 for fuel and power; while $100,000 is expended for other miscellaneous expenses of manufacture. The total value of the products of bake shops and factories is $650,000,000 annually, thus making the value added by manufacture of the total material of baked products $300,000,000.

Bakery Shops. Twenty-seven thousand one hundred and twenty-four bakery shops produce more than one-half of the baked products manufactured. The bake shops are principally operated by proprietors employing one helper, a large number of women proprietors making a living in this way.

The equipment of the shop is usually: one portable oven holding from 50 to 150 loaves of bread; a cake machine used for mixing cake batter; mixing bowls; a few racks, and other miscellaneous equipment, the bake shop usually being in the rear of the building and the products sold in the front by the owner to his retail trade. These shops bake each day from 1 to 3 barrels of flour, making a general line of baked products, usually bread, coffee cake, layer cakes, sponge cakes, rolls, biscuits and buns.

Methods. The methods employed in these bakery shops are usually according to the experience of the baker or proprietor.

Bread is usually made using practical judgment as the only guide, so that when a dough is stiff enough no more flour is added, or when the baker considers the dough ready or ripe it is divided and molded into loaves. The temperature of the dough is gauged by feeling with the hand. Cake

and other mixes are similarly thrown together according to judgment, using the quart measure as the main basis of figuring amounts.

Some of the usual mixes and methods are as follows:

Bread.

50 lbs. flour	100 lbs. flour
3 qts. water	6½ qts. water
1 lb. yeast	1 lb. 12 oz. yeast
12 oz. salt	1½ lbs. salt
1¼ lbs. sugar	2½ lbs. sugar
3 oz. milk powder	6 oz. milk powder
1 lb. lard or compound fat	1 lb. lard or compound fat

The yeast, salt, sugar, and milk are dissolved in the water, and the flour worked into a stiff dough. The water is taken at such a temperature as to obtain the desired temperature of dough (85° F. on cold days in a cold shop, 79° F. on a warm day in a warm shop, 81° F. being the best temperature to maintain, providing the dough does not cool off or warm up to outside temperature). The dough is usually placed in a wooden trough covered with a board or sack, and is allowed to expand and thus rise to the top of the trough (usually until it will just about drop of its own weight), three times, when it is considered ready and in a condition to make the best bread.

The dough when first mixed is tough and rubbery. As it expands in the trough (rises and gets older) it gets more and more short until the dough breaks off readily instead of pulling as elastic. When a definite degree of shortness is reached it usually gives the best bread. Too great an age gives coarse, sour bread, too little age results in coarse, tough and small-volumed bread.

Whole Rye Bread. (Pumpernickel.) For 1 barrel of whole rye flour of 196 lb., about 90 lb. of water; 2½ to 4 lb. suet; about 2 lb. cane sugar; 1 lb. compressed yeast. The dough is aerated by employing sour dough for leavening, the leaven being daily mixed with more dough, the mass ripening again in twenty-four hours, or over night to more leaven; the process being kept up indeterminately often without adding yeast, as this develops in the sour dough.

Mixed Rye Bread. Generally rye flour is mixed with from 25 to 50 per cent of wheat flour, in order to improve color and aeration. Naturally the characteristic quality of rye bread is lost with a larger percentage of admixture.

Rolls. The same material as for wheat bread is used, with larger quantities of milk and fat shortening.

Cake. Wheat flour 10 lb. and milk or water 5 lb. or in the proportion like wheat bread; butter or lard 2 lb. per 10 lb. of flour; eggs, 2 lb.; a little salt; sugar, 2–3 lb.; baking powder, 2 oz. or less.

Soda Biscuits. Wheat flour and water; salt and yeast are mixed as

in the manufacture of wheat bread. The dough is allowed to ferment for about twenty hours, in order to break down the gluten of the wheat entirely. During this prolonged fermentation, lactic acid acidity develops, this being the agency to break down the gluten. Now a sufficient amount of bicarbonate of soda is added to neutralize the acidity; at the same time lactic acid and the bicarbonate of soda, both neutralizing one another, so that no acid taste nor soda taste is noticeable. In order to invigorate the fermentation a small amount of malt extract is employed in mixing the dough.

For sweet soda biscuits and graham biscuits, an adequate amount of sugar is used in mixing. The finished dough is rolled out in flat sheets of the desired thickness. These are cut or divided, the dough pieces placed in pans and baked.

Factories. America now contains about 1800 factories for the manufacture of bread, cakes, pies, biscuits and crackers. They bake less than half of the bakery products manufactured and sold, representing considerable capital and employing large numbers of men. They are equipped with extensive and complete machinery which is housed in buildings erected exactly suitable for the purpose and handle enormous amounts of materials.

Bread Factories. There are 1400 bread factories in America whose chief product is white bread and rye bread. Bread factories very often manufacture rolls and fried cakes as well as box cakes.

The bread factories of America usually manufacture one of the following types of bread: English type cut tin loaf; ordinary cut tin loaf; American homemade style tin bread; restaurant sandwich tin bread; French type sandwich bread for restaurants; American homemade bread.

Bread-factory Economics. Modern bread factories in America, equipped with costly and intricate machinery, have attained to the dignity of factories with a daily consumption of flour ranging from 10 to 200 barrels, and a daily output of over 3000 to 50,000 loaves of bread, a few even reaching 200,000 loaves per day. Bread, rolls, and cakes are all produced on a large scale and of such quality and price that it is no longer an object of the housewife in our larger cities to have the baking of these products done at home. Wheat bread is the chief product of the modern bakery, then rye bread, rolls, and cake. Over 20,000,000 barrels of wheat flour are annually consumed by bread factories in the manufacture of wheat bread; 500,000 into rolls; 500,000 into cakes. The amount of rye flour made into rye bread and used for other purposes is approximately 2,000,000 barrels.

Bread-factory Construction and Equipment. Space does not permit to go into the details of the various types of machines and apparatus, ovens, proofers, troughs and other accessories of a modern bakery. Changes in construction and equipment have become necessary from time to time as baking technology progresses; as changed values are given to materials

and processes; as new methods or processes are introduced, or new requirements are made on the baker to meet Government or Food Administration regulations.

The structure is usually of brick—two stories and a basement, with large windows, so that the process of bread making can be seen from the outside. Spacious offices, shipping rooms, retail sales rooms, wrapping rooms—the bread is never touched by hands except those of the white-gloved bakers who pack bread for shipping—separate sanitary lavatories for all departments, mixing rooms, dough dividing, and molding machinery rooms, proofing and oven rooms, boiler and oven-firing rooms are all well ventilated and lighted so that there is no dark corner in the entire plant. All interior walls are kept white with enamel or granite paint, also the white framework of all machinery used, including the proofing cabinets, while the brick or metal face of the ovens is white glazed or glass enameled or white tile. Everything is done with a view to add attractiveness to the place, so as to educate the visitor to give preference to the modern factory output, as everything suggests sanitation and wholesomeness.

The mixing room is generally on the second floor, adjoining the flour warehouse, in which a considerable quantity of flour is always kept on hand to insure proper aging, since new flour will not give the best loaf. The flour hopper, with a capacity of five barrels of flour or less, which is to feed the mixer, is portable, and may be conveyed to the various bin cone sifters from which the supply is taken. The hopper is run to one of the mixers, emptying its contents into it, and returning to the same or another bin for another charge of flour. Into the mixer are carefully weighed the flour; the water; the shortening (lard or vegetable oil); salt; yeast previously dissolved in water, sugar; usually in the form of cane sugar or malt extract. Metal dough troughs on wheels receive the mixed dough, which is given time to ferment (usually 5 to $5\frac{1}{2}$ hours), in a specially constructed dough room in which the temperature and humidity are automatically controlled. The dough rises in the dough trough and is kneaded or punched three times. Then the troughs are wheeled to a chute in the floor and let down to the dividing machine, which is so arranged that it can cut any loaf from about 10 to 40 oz. The dough is carried to the rounding machine automatically where it is rounded into a ball and thence to the proofer, where it rests for about ten minutes in a temperature of about 85° F. The pieces of dough are now let down by a conveyor to the molding machine where they are molded into the form of loaves, which are placed in the bread pans. These are loaded upon conveyor racks and wheeled into the proof cabinets, where they remain from twenty to fifty minutes, according to the individual judgment of the baker, in an atmosphere of steam, at about 90° F. The conveying racks are rolled from the proofer to the oven, which, according to capacity, receive a charge of 250 to 500 loaves of bread, the average baking period being thirty-five minutes, after which the loaves are taken out by a long, wooden pole, formed at the end

like an oar blade, on which the pans are caught, an implement called a peel. Other types of ovens called rotary ovens receive the pans automatically. The most advanced ovens are the traveling ovens of large size in which the pans enter one end and pass on a movable hearth during baking and then issue out at the other end. The loaves are then loaded on the wheeled racks, or are dumped down chutes and, after cooling, are packed into cartons or paraffin paper and reach the delivery truck-wagon to be shipped or delivered to the trade.

Baking Process. *Mixing.* In making wheat bread on a large scale the various ingredients, flour, water, salt, sugar, malt extract, lard, and yeast are mixed in a mixing machine, the yeast being previously dissolved by mixing it in water. After mixing thoroughly to a homogeneous mass, the dough is placed in a dough trough, constructed of wood or sheet iron, the dimensions of the trough varying from 2 to 3 ft. in width; depth about the same; length from 5 to 10 ft.

Dough fermentation gradually sets in and progresses for about 2 to $2\frac{1}{2}$ hours, to the extent of causing the dough to rise in the trough to treble and more its original volume. Now the dough is punched in the trough or kneaded and worked until it has fallen back to nearly its original volume; it is again left to rise. The second dough fermentation being finished in about $1\frac{1}{2}$ hours, when it receives its second punch, that is, it is again kneaded and worked until it has fallen down. It is again allowed to ferment, this time for about forty-five minutes, when it receives its third punch, and is then ready, after about ten minutes more, to go to the bench.

Dividing. (Bench work.) In hand-operated bakeries, the dough is placed on a large, flat, oaken table, cut into pieces, weighing 18 oz., 26 oz., etc., according to weight of bread desired. These pieces are properly molded in loaf shape and are placed into the bread pans. These are placed on racks.

Proofing. These racks are conveyed on rollers to the steam, or proofing cabinet, usually constructed of sheet iron, filled with an atmosphere of steam, where the pans are left for about fifty minutes. The dough here achieves its last rise, filling the pans quite to the level of the rim, more than doubling its volume. Then they are taken out and placed in the oven.

Baking. Baking requires about thirty-five minutes, which is usually the time of a bake. Here the dough piece increases its volume once more, mainly through expansion of the gases caused by the high temperature of the oven. This is the *spring*, the proper volume of which is very important to the quality of the bread. After baking, the spring should be one-fourth of the entire contents of the pan, increasing the volume of the bread by one-fifth of the whole loaf.

Finishing. Many types of bread, as Vienna bread, are washed with a solution of starch immediately after baking to give the finished loaf a glossy crust. American bread is often wrapped in waxed paper and sealed with self-sealing wrapping machines. A practice is coming into

use of cooling bread in predetermined atmosphere as water vapor, or other gases, which treatment causes the bread to remain fresh for a longer period of time.

Bread-making Methods

Straight Dough Method. The proportions of materials used in the manufacture of wheat bread are as follows:

Flour	196 lbs.	392 lbs.	588 lbs.
Water	110	230	353
Sugar	3	6	9
Malt extract	2	3¾	5½
Salt	3	6	9
Yeast	2½	4½	6½
Lard	2	4	6
Time of mixing	12 min.	18 min.	22 min.
Time to first punch	2 hrs. 30 min.	2 hrs. 30 min.	2 hrs. 30 min.
Time to second punch	1 hr. 30 min.	1 hr. 30 min.	1 hr. 30 min.
Time to third punch	45 min.	45 min.	45 min.
Time to bench	15 min.	15 min.	15 min.
Number of No. 1 loaves	288	600	875

The above columns give the formula for three sizes of dough ranging from 1 barrel to 3 barrels of flour. Many formulas have been devised and are practiced, some using additional materials as milk. The materials are employed at such a temperature as to obtain a resulting dough temperature of 81° F.

Mixing. All of the materials are mixed at once in the dough-mixing machine in the following order: Water, sugar, malt extract, salt, and some flour (substitutes if used). After a homogeneous mass has resulted the dissolved yeast is added and thoroughly mixed. Then introduce into the mixer all the remaining flour. The dough is mixed eighteen to twenty-five minutes according to type of mixing machine employed.

Fermentation. The dough is then dumped into a dough trough and allowed to ferment. The dough rises during fermentation and comes up to a certain height in the dough trough (nearly ready to fall from its own weight), and is then punched down (cut down with knives or punched down). This is repeated three times, the first punch taking place about 2½ hours after rising, the second punch taking place 1½ hours after the first punch, and the third punch taking place forty-five minutes after the second punch. During fermentation the dough changes its physical character. Directly after mixing, it is rubbery and tough and if molded into loaves would make a tough small-volumed loaf. After three punches the dough is properly aged and is elastic and soft in its character. It breaks off with a quick pull by the hand—a dough receiving too great an age will be very short and unelastic and will result in a pale, heavy and coarse loaf. The dough is then taken to the dividing machine and divided

into loaves of proper weight, molded and placed in pans for proofing. The 1-lb. dough piece rises in the pan to a proper volume in forty-five minutes and is baked in thirty-five minutes to a rich brown color.

Sponge and Dough Method. In a sponge method about one-half of the flour and water and yeast are first mixed into a dough and then allowed to ferment to the first punch. It is then thrown back into the mixer and all other material added and then mixed into a dough and allowed to ferment as usual. A number of variation of methods is possible by this method. Some bakeries use a larger quantity of water in the sponge, thus making a soft sponge. Others vary the quantity of material used in the sponge using one-quarter or one-third of the total flour in the sponge.

Ferment Sponge and Dough Method. Several bread factories make a ferment with potatoes and malt extract or other yeast-nourishing media, and then mix in flour and other materials to make a sponge and later make a dough in the usual way.

Bread-baking Materials

Flour is the chief material entering into the composition of a loaf of bread. Considerable work has been done by chemists the world over to establish methods to ascertain the baking value of flours by scientific methods. Each chemical component has been investigated and the moisture, ash, fat, gluten and acidity and other determinations have been carefully made in an endeavor to determine the baking properties of such flour. Recently the gluten content has received considerable attention. Formerly the ash content was considered of greatest importance. It is generally accepted that a flour containing a high gluten content will result in a loaf of large volume per weight of bread, and a flour low in gluten content will result in a loaf of small volume per weight of bread. However, it is also generally known, both by chemists and bakers, that it is difficult to judge the baking value of flour in cases where two samples both have a low gluten content or both have a high gluten content. Often times a flour containing only 8 per cent gluten will have better baking qualities than one having 9 per cent gluten. Also many cases are known in which a flour containing 12 per cent gluten will have poorer baking values than one containing only 11 per cent gluten. Flour laboratories generally check the results of the chemical analysis by a scientific baking test. We have found that, in order to determine as nearly as possible the true baking value of a flour, various tests are helpful, such as the expansion tests and dough-softening tests. The scientific baking test, while probably the most helpful, is still crude, since influenced by so many varying factors. The necessity of checking a scientific determination, such as the chemical methods employed by a crude test, has caused much dissatisfaction amongst both flour chemists and bakers. We learned a few years ago of a new method for determining the baking value of flour by a highly scientific

method that was being developed in the Carlsburg Laboratories of Biological Research, in the City of Copenhagen, Denmark, by Dr. Jessen Hansen. This method is the determination of the hydrogen ion concentration of a flour solution by an electrical apparatus. It has been very useful, but it is also lacking in ascertaining definitely the baking value of any flour.

Due to the importance of this question for both the baking industry and science, the writer personally entered into researches to determine the factors influencing the quality of flour for bread-making purposes. The question was studied:

1st. From the viewpoint of the effect of living organisms (microörganisms) that exist in flour, and which develop during dough fermentation.

2d. The effect of natural enzymes of both young and old flour during dough fermentation.

3d. The relation of the chemical composition of flour to the enzymatic and bacterial activity.

The following conclusions were derived:

1. That the baking value of flour is influenced considerably by the number of microörganisms present therein. The kind of microörganisms in the flour also are of considerable importance and largely affect dough-making operations.

2. During aging the bacteria in the flour increase in number, and have a liquefying effect on the gluten, altering it in the direction of greater "ripeness."

3. New flour has a greater activity of proteolytic enzymes than old flour, but a smaller number of active microörganisms.

4. The activity of the various bacteria existing in the flour causes various faulty properties in the bread, such as holes and streaks.

Flour contains many living organisms so small that they are invisible to the human eye, and can be detected only with a high-powered microscope. Experiments have demonstrated that these small organisms (microörganisms) influence the baking value of a flour to a very large extent. Some flours contain only a comparatively small number, while others contain relatively large numbers of these living organisms. New flour possesses comparatively few, while old flour possesses a much larger number. The author accredits the observed differences in the baking values of new and old flours, in part, to the number of microörganisms and their action and effect upon the gluten of flour during its aging and also during the fermentation stage of the dough. Flour containing a small number of microörganisms must receive a different treatment during dough fermentation than flours that have a large number of bacteria—all other factors such as chemical composition and enzymatic activity being equal.

Bread doughs made with the flour containing a large number of micro-

örganisms will require less actual fermentation than those with only a small number of microörganisms. This then offers an explanation for the observed facts in actual practice. New flours require a longer fermentation and more yeast, or the addition of some proteolytic enzyme to the dough, in order to ripen the gluten.

Besides the actual number of microörganisms existing in a flour, we have observed that the actual type also largely affects bread-making operations. Some types of microörganisms existing in the flour have been found to be beneficial, and the bread properties are improved by their action on the flour during dough fermentation. Again, we have found other types of microörganisms which destroy the adhesive properties of the gluten, resulting in holes in the bread or a lack of " spring " in the oven.

Examinations have shown that various types of mold existing in the flour cause trouble during dough fermentation, besides resulting in the premature appearance of mold on the crust of bread after baking. Putrefactive microörganisms will cause disagreeable odors in the bread after baking by breaking down the gluten and other protein substances into a slimy putrid mass. Other organisms of the well-known yeast family are also in the flour. In this family there are types which aid in producing a loaf of good properties. Other yeasts exist that do not cause any injury during bread production other than developing by using up much of the yeast food, thus depriving the culture yeast of this nourishment. The injurious types of this family, the wild yeasts, which exist in the flour, can cause considerable damage during dough fermentation, such as unpleasant flavors and large holes in the resulting bread. The causes for successful as well as faulty bread production we are now able to trace to the activity of numerous microörganisms of various types. A further study will demonstrate which microörganisms cause the various miscarriages in bread production.

Other factors which influence baking operations to a large extent are the soluble ferments known as the enzymes. Our researches have led us to believe that flours when newly milled have considerable proteolytic enzyme activity. This enzymatic action decreases with the age of the flour. For this reason new flours become soft and runny when in the dough stage, while dough made with aged flour retains its consistency through the fermentation stage. The activity of this proteolytic enzyme (peptase) aids also in altering the gluten of the new flour during the aging thereof.

Both the enzymes and microörganisms have their effect principally upon the constituents of the flour. They alter the proportion and character of each ingredient of the flour. Thus it is not sufficient to know the chemical analysis of the flour alone, but one should also be able to determine its enzymatic content, as well as the number and kind of microörganisms in order to judge scientifically the baking value of a flour.

The water used in baking operations may be classified from several points of view:

a. According to the amount of mineral substance contained in them: 1. Hard waters; 2. Soft waters.

b. According to organic substances, products of putrefaction or organisms they contain: 1. Pure waters; 2. Impure waters.

c. According to their origin: 1. Rain water; 2. Condensed or distilled water; 3. Lake water; 4. River water; 5. Spring water; 6. Shallow well water; 7. Deep well water.

In estimating the value of water regard should be had to its availability for: 1. Milling; 2. Baking; 3. Yeast propagation; 4. Feeding boiler; 5. Washing troughs, barrels and vats; 6. Cooling; 7. Watering horses.

According to the purpose for which it is intended, water is judged by the amount contained in it of: 1. Mineral substances; 2. Living organisms; 3. Organic substances.

Water takes up various constituents on its passage through the soil. Some are soluble directly in water, others are made soluble by carbonic acid which the water takes up while falling through the air in the form of rain, or from the soil. The solvent action of carbonic acid is noted with reference to carbonates of lime and magnesia, which, being encountered in the soil in an insoluble form, are converted into soluble bicarbonate by the carbonic acid of the water.

The substances contained in water in general are: 1. Gases—air (oxygen), carbonic acid, sometimes sulphureted hydrogen (noticeable by its odor); 2. Organic substances and microörganisms and the products of decomposition set up by them as ammonia, nitrous and nitric acids (all of which are undesirable in baking operations); 3. Mineral constituents: *a.* Lime, in the form of bicarbonate of lime, sulphate of lime (gypsum), chloride of calcium. *b.* Magnesia, in the form of bicarbonate of magnesia, sulphate of magnesium (Epsom salts), chloride of calcium. *c.* Sodium, in the form of chloride of sodium or common salt, sulphate of sodium or Glauber's salt. *d.* Potassium in the form of chloride, sulphate or bicarbonate of potassium. *e.* Iron, in the form of bicarbonate of iron. *f.* Aluminum, in the form of hydrated oxide of aluminum. *g.* Salicylic acid.

Action of Constituents Held in Solution. If the substances enumerated occur in the water in considerable quantities, their action is felt in the following manner:

1. Organic matters and microörganisms promote putrefaction and mold.

2. Ammonia, while harmless in itself, indicates the presence of putrefying matter and bacteria of putrefaction.

3. Nitrous acid hinders saccharification, is a strong yeast poison, may cause disturbance in fermentation and, being a product of ammonia oxidation, indicates the presence of products of putrefaction. In fermentation at high temperature, the head may acquire an offensive odor, as of chlorine.

4. Nitric acid is injurious only if present in quantities. In the presence of denitrifying (reducing) bacteria, nitric acid may be transformed into nitrous acid, which will then exercise its pernicious influence.

5. *Chlorine.* Large amounts of chlorine, particularly if coupled simultaneously with a large amount of ammonia, make a water suspicious, as it suggests the possibility of infection by drainage, particularly sewage, animal or human excrement and bacteria. The chlorine compounds have the following action: Sodium chloride acts as a germicide during dough fermentation, exerts a beneficial influence on the elasticity of the gluten. Magnesium and calcium chlorides have a similar action in dough fermentation. The employment of a water rich in these salts, for dough making, will result in a finished bread with a hard taste.

6. *Calcium.* Calcium sulphate is desirable for baking, particularly for producing a bread with white crumb. During dough fermentation it aids in rendering soluble the proteins of the flour.

7. *Magnesium.* Magnesium carbonate. Same effect as calcium carbonate.

8. *Sodium.* Carbonate of soda in sufficient quantities to make a water alkaline is undersirable, even in small quantities. In baking it weakens the enzymes as diatase and peptase, and thereby delays the ripening of the dough. It gives dark color of crumb to the bread. It neutralizes the lactic acid of the dough, and hence the dough is more exposed to the action of microörganisms, increasing the liability to bacterial odors and discoloration.

9. Iron in larger quantities produces an off-colored, gray bread. It has a detrimental effect on the yeast. It colors yeast dark and gives an onion odor to bread, on account of its effect upon the yeast.

For Baking. Moderately hard water with a moderate amount of sulphate of lime (gypsum), sulphate of magnesium (plaster of Paris and common salt), free from iron; for a very pale bread crumb, poor in carbonates. The purity of the water is to be regarded, for the microörganisms therein will develop off odors and tastes in the bread. Alakalin waters are harmful in baking, since they neutralize the acidity of a dough, thus affecting the action of the enzymes (natural ferments).

Improvers

Modern Baking has brought with it a score of additional commercial substances which, when added to the bread dough, are supposed to effect considerable advantage in bread-making. Due to the large number and variety of these so-called improvers, we believe that the scientific principles underlying flour improvements for bread-making, generally, should be familiar to those engaged in the baking industry so that these improvers may be used more intelligently and also to place the baker in a position to judge the value of these substances with greater accuracy.

The common interpretation of the word "improver" in the baking

industry is " some substance which, when added to the dough will effect an improvement, either in the economic production of the bread or in the bread itself." For instance, improvers may increase the water-absorbing power of a flour or lessen the time of fermentation, or effect a saving in the amount of yeast. Other improvers produce much greater color of the crust, or whiteness in the crumb or effect a larger volume per weight of bread, or may cause an improvement in the flavor.

Thus, it is convenient to classify those various items which influence directly the economic production of the bread and which may be altered by added improvers, and it is also convenient to classify those properties of the bread itself which may be effected by added improvers. The points to be considered in the economic production of bread are as follows: 1st. Time of dough fermentation; 2d. amount of water absorbed; 3d. amount of yeast required; 4th. amount of wheat flour necessary; 5th. amount of fermentation losses.

Any decrease in the time of fermentation will effect the economic production of a loaf of bread, inasmuch as it lessens the amount of labor required and decreases the time of use of the various dough-handling equipment, thus allowing a larger bread production with the same equipment. Certain substances may be added to the bread dough which will ripen the gluten of the flour in less than normal time, thereby conditioning the dough for the baking thereof in a much shorter than normal time and would, in that case, lessen the economic production of the bread, giving the added substance value accordingly.

The economic production of bread is greatly influenced by the amount of water incorporated into the dough, a large proportion of which is retained through the baking stage and remains in the bread. Bread sold by weight will, in this case, be much more economically prepared than if less moisture were contained in it. Several substances may be added to the dough to allow a greater addition of water, either by its influence upon the water-absorbing capacity of wheat flour or by the greater water-retaining capacity of the added substance itself.

Yeast not alone aerates the dough, through the evolution of carbonic acid gas, but it also excretes a substance, termed by the biochemist " endotryptase," which acts on the glutinous substances of the dough in such a manner as to modify it in the direction of greater elasticity, that is, " ripen " it. Certain added substances containing a similar principle to " endotryptase " of yeast will ripen the dough in a like manner, independently of the yeast itself. Still other added substances will have a stimulating and invigorating effect on the yeast organism, so that it influences in a magnified degree, thus allowing a decrease in the actual added amount of yeast by which the economic production of the bread will be effected.

Wheat flour is usually the most costly single item of a bread dough. It is required usually on account of the elastic material it contains. This glutinous substance must be modified in the direction of greater elasticity

by effecting its partial disappearance by solution. Several substances may be added to bread dough that can replace the wheat flour in part, without seriously injuring the elasticity of the resulting dough, which substances are sometimes less expensive than wheat flour, and their addition therefore influences the economic production of the bread.

Certain losses occur during dough fermentation and during the baking of the dough. The fermentation losses are usually in the form of volatilizable alcohols, and carbonic acid gas. The more rapid the fermentation phenomenon, and the longer the time, the greater will be the loss from this cause. Substances may be added to bread doughs which would tend to lessen the amount of actual fermentation, thereby saving the fermentation losses, and which would also decrease the loss occurring during the baking of the dough.

Yeast, *sugar*, *salt*, *malt extracts* used in baking bread to obtain the gas which aerates the dough and bread the yeast fermentating the sugar or malt extract into carbonic acid gas and alcohol, the rate of fermentation being influenced by the quantity of salt. The subject of fermentation is an extensive one and is considered under baking technology.

Historical

Baking is probably the very oldest industry man engaged in. Wheat and barley, the oldest cereals known to have been cultivated, have been found together with the plowshare fashioned of wood and the stone hand-mill consisting of a hollowed stone ball-shaped crusher among the remains left by prehisotric man, deposited in his burial places or found embedded in the earth over or near which he had his dwelling places. These implements, together with arrow heads, spear heads and battle axes, all of flint or stone (Stone Age of Man) gave evidence that man at that time was unacquainted with the use of metal, and that his primitive culture must have dated back some five to ten thousand years before the beginning of the Christian era.

Food of Primitive Man. While the finding of the remains of wheat and barley and the plowshare gave evidence of agricultural pursuit, the bones of domestic and wild animals and the remains of clams and oysters indicated that his diet was quite a variegated one; that he employed the domestic animals to ease his own work, while remnants of woven fabrics, especially from flax fiber, indicated that he had learned to cultivate plants for other than food purposes.

Oldest Form of Baking. The oldest bread was made in the form of cakes or fritters, simply prepared by mixing wheat or barley meal to a batter with water and milk, and baking these batter cakes of, maybe, the size and form of our present-day griddle cakes, on hot ashes or over red-hot coals, or a hot stone which represented the first bread pan and oven combined. Salt was probably the only other ingredient besides the meal and

water and milk, as there certainly was no baking powder and yeast was not used until brewing beer from germinated barley had become known, though sour-dough bread was probably as well known as sour-milk products.

The Egyptians, as the remains found in the tombs of the pyramids show, had perfected both baking and brewing 1500 years before the beginning of the Christian era, and the Old Testament makes mention of a mill known to the Assyrians. These occupations had become organized industries. In Egypt, in brewing as well as in baking bread, the grain was crushed, mixed with water to a dough and fermented by the addition of fermenting bread mash, which was then baked. The fermented beverage was simply prepared from slightly sprouted barley or other grain, by crushing it, mixing with water to a mash, slightly baking the dough, breaking the bread, making a mash with water and adding fermented mash once more for fermentation. The fermenting beverage then supplies the yeast for baking.

From Handicraft to Industry. How baking developed from a simple handicraft, with a stone hand-mill furnishing the grist or meal, and the baking of a batter of meal and water on ashes, or over red-hot coals, or on a hot flat stone, into a highly developed art, through the ages, and then into one of the most important industries engaged in by man, would, indeed, form an interesting story for this article, would space permit. Man learned to use bronze metal to fashion his tools, utensils, weapons, long before he had found iron. The bronze age of man, which lasted probably upward of a thousand years, preceded that of the iron age. In this period iron took the place of bronze and stone. Unlike the use of bronze, which had spread westward and northward from Asia and Africa, iron was first discovered and made use of by the Celts in northwestern Europe, from where it spread eastward and southward.

Primitive Baking Pans. Flat sheets of iron, rounded and provided with a wooden handle, early in the culture of our European ancestry took the place of the hot stone, hot ashes or coals in baking flat cakes, and this led naturally to the development of the bread pan and the employment of the baker's oven, which, in the time of the Egyptians, was fashioned out of clay with a flat bottom and arched roof, of varying size for household and shop use.

The Technology of Wheat Bread Baking

Quality, Character and Properties of Bread. Before selecting and weighing the materials for the purpose of baking operations the baker should clearly understand the requirements the finished product is to meet. Every operation he carries out should be understood with a knowledge of the influence it may have in shaping the quality, character and properties of the bread as desired.

Bread has *quality* if it possesses recognized merit and meets the requirements of the trade.

Bread has *character* if its properties conform to those of a recognized standard or type. Typical breads vary widely as to their distinctive properties. The types are as follows:

English Type Bread. Principally large-volumed loaves of many shapes; usually characteristic of a community: London cottage shape predominating, small topped and standard cottage (see Shapes). Other types of bread: Notched cottage; Coburg plait or collas; double notched cottage; tin cottage; notched tin cottage; batch cottage; Dutch cottage; brick loaf; twist; split cob.

All of this bread is crusty, baked in hot oven, is usually well browned with excellent bloom ranging from light yellow to deep brown. Texture is cream white with beautiful pile and dense but light texture; perfect grain. Tin bread varieties are as follows: Sandwich tin; bon tin; coronation loaf; oval tin; cut oval tin; split tin; standard tin; long tin; split long tin; cut long tin; fancy tin.

The bread has a wheat flavor, sweet taste and nutty aroma; very wholesome, readily digestible. The bread is of average gluten content; good fat content; high in mineral ingredients; high water content; high in salt; made usually with straight dough method, in machine bakeries.

French Type Bread. Is usually made of very light volume compared to its weight, of long shape usually notched; thick crust and is light yellow in color with slight bloom; texture is velvety and regular white in color and very neutral taste. Is wholesome and very digestible but has little zest. Its composition is high in protein but low in fat, with little salt, made usually with a sponge and dough method and in a Vienna type mixing machine; using French wheat flour with some English and Hungarian wheat flour mixed in.

Irish Batch Bread. Baked on solid oven bottom, by baking dough pieces tightly together in hexagonal formation.

Vienna Bread. Neutral taste, thick crust, dark color of crust.

American Type Bread. Is of average volume; with standard shape of pan; shape is cut or burst or split; sweet taste in West, tart in East, with cheesy taste in South; neutral in Central States; good bloom and color.

The Homemade Type. Rough in appearance, fine texture, made of doughs containing milk.

Properties. The properties of bread must be considered from the viewpoint of its crust and crumb. The important properties of the crust are the taste, color, bloom, thickness, softness and digestibility. The properties of the crumb are volume per weight of bread and shape; the color, pile, grain, texture, taste, and velvetyness of crumb; the taste, flavor and aroma; the zest, palatability and appetizing qualities; the wholesomeness and digestibility.

The Volume. Volume is the measure of the space occupied by the finished bread compared to its weight. It is usually measured in cubic inches employing one pound of bread for the unit of weight. The materials,

methods and processes employed affect the volume considerably. Certain types of bread are wanted to be light (large volume for its weight); others are desired more dense.

The volume per weight of a loaf of bread depends largely on the size and number of fermentation gas cells and of the thickness of the walls of these cells. The quantity and quality of the elastic material in the bread dough is largely responsible for the conditions of these cells and any material added to the dough which will modify the glutinous substances of the dough in the direction of greater elasticity, so as to allow the production of a large number of small thin-walled fermentation gas cells will cause an improvement in the volume and shape of the bread. The number and size of the fermentation gas cells is also largely dependent on the number and activity of the individual yeast cell groups existing in the dough, and any principle which tends to increase the distribution of the invigorated and activated yeast as to make it separate into individual cells or very small cluster would effect a similar improvement in the bread.

Shape. The shape of a loaf of bread is usually dependent upon the pan in which it is baked, the method of molding or of packing the dough piece in the oven, as is the case of various kinds of Irish bread.

Color of Crust. The depth of color on the exterior of the bread is caused by the action of the heat on the organic matter of the product, due to the carbonization of the various ingredients, chiefly the caramelization of the sugar.

The color of the crust is dependent largely upon the amount and kind of caramelizable sugars existing in the bread dough at the time of baking. Wheat flours contain very little natural sugar of this kind and various substances containing this principle may be added to bread doughs which will give a deeper color to the crust of the resulting bread than would be obtainable by the use of cane sugar alone.

Bloom. Bloom is the shading of color of the crust from light to dark, causing oftentimes the appetizing appearance of a loaf of bread.

Color of Crumb. The color of the crumb of a loaf of bread is influenced largely by the way light strikes the texture and upon the physical condition of the starch and nitrogenous material after baking. During the baking of the dough the soluble albumins coagulate into white flaky masses. Certain substances added to bread dough either act in such a manner as to render the starch and nitrogenous material white in appearance or effect the production of a comparatively large amount of albumins in the dough.

The *grain* and *texture* and *velvetyness* of the crumb of a loaf of bread is dependent directly upon the number, size and uniformity of the fermentation gas cells and upon the thickness of the walls of these tiny cells. These conditions are produced largely by the yeast and elastic properties of the glutinous substances in the dough. A large number of active invigorated individual yeast cells evenly distributed will render a large

number of small, round fermentation gas cells with very thin cell walls. Any substance added to the dough which will tend to place the yeast in this form and will aid the production of a uniform texture and will influence the quantity of albumins in the dough so as to render a white, flaky crumb, may be considered a very beneficial improver.

Taste, Flavor, Aroma. The verdict of the masses on the natural taste, flavor or aroma of flour is that it is insipid and undesirable. These natural flavors are so altered in the baking processes as to be exceedingly desirable and pleasing. The production of flavors is generally effected by the combination of the alcohol and natural acid of the dough creating a class of substances known as "esters." Much improvement is obtainable in the direction of improved flavor by incorporating into the dough substances which themselves contain desirable esters, or will effect the production of esters during the baking processes.

Palatability and Appetizing Qualities. The human palate recognizes hard or soft foods, smooth or rough foods. Appetizing qualities and palatability are largely a matter of education and culture of the individual. The palate of the American masses generally is believed to prefer soft, smooth foods. Wheat flour bread tends to produce a loaf which would strike the palate as hard and rough. This quality increases as the bread becomes older, giving the generally recognized stale influence in the palate. To the bread dough substances may be added which will result in bread of the soft, smooth palatability and appetizable qualities.

Digestibility is the rate with which the bread is altered from insoluble material in the digestive system.

Wholesomeness and Nutritive Value are the measure of the amount of tissue and energy building material the weight of unit bread contains.

Zest is the invigorating effect caused by consuming bread, usually dependent upon the amount of carbonic acid gas remaining in the porous structure of the bread.

Composition of Bread. The composition of bread is as follows: protoplasm, enzymes, proteins, carbohydrates, acids, fats, esters, alcohols, oxides of carbon, mineral matter, water.

Protoplasm. Many forms of bacterial life survive the baking temperature and remain in the bread after baking, causing mold and the disease in bread called rope; and acid bacteria causing sourness; and various others. The structure of these forms of bacteria is chiefly protoplasm.

Enzymes. While all of the original enzymes existing in the materials which enter into bread dough are destroyed after baking, the various forms of bacterial life which survive or which impregnate the bread after baking contain active enzymatic principles which affect the ingredients of the finished bread in various ways, such as liquefying the gluten or saccharifying the starch or causing rancidity of the fats.

To this class belong such specific enzymes as peptase, diastase, inver-

tase, maltase, zymase, all of which cause changes in bread dough if present in sufficient amounts, and are the least understood of any of the chemical groups.

Proteins. The proteins are the nitrogenous principles upon which the food value of bread depends. They exist in bread after baking in the form of insoluble protein, both the natural globulin and the coagulated albumin derivatives as well as some uncoagulable proteins, as amides and amino acids.

Carbohydrates. The carbohydrates in bread are celluose of the bran; raw starch, gelatinous starches, soluble starch; dextrine, as amylo dextrine, erythro dextrine, achro dextrine, which affect the crust of the bread, large amounts of dextrine causing a hard, brittle crust; sugars, as saccharose, maltose, dextrose and lactose. After baking gelatinous starch forms the greater bulk of the bread and aids in producing the white appearance of the bread.

Fats. Fats enter the bread usually through the added lard or compound fats containing stearine, palmatine and oleine as the chief fatty principle.

Esters. Esters are those chemical compound ingredients in bread which give it its characteristic flavor.

Alcohols. The alcohols existing in bread are formed through the fermentation of the sugars which are not volatilized in the baking, these being chiefly the higher forms of alcohols, such as glycerine, amyl alcohol, butyl alcohol, and some ethyl alcohol.

Mineral Matter. The mineral matter is the amount of mineral ingredients existing in the bread and is an important part of the nourishing qualities or tissue of building material.

Carbon Dioxide. The carbon dioxide existing in bread is also a product of the fermentation of the sugar and exists in the cells giving the zest-producing qualities of fresh bread.

Water. Water is one of the chief components of bread, starch being the chief ingredient. Water composes about 40 per cent of the weight of fresh bread, slowly evaporating and diminishing as the bread gets older and stale.

Baking Operations

Oven Operations. *Peel ovens* are the simplest type of baking ovens, in principle being a heated chamber into which the bread is placed with long poles (peels) and allowed to remain on the floor of the oven until baked.

Rotary ovens exercise the principle of a heated chamber into which there revolves a rotating hearth or oven bottom. The bread is placed on the revolving hearth through a small opening and removed when baked. The hearth revolves in conformity with the speed required to load and unload.

Traveling ovens are built on the principle of a large heated chamber through which passes a moving hearth on an endless belt. The bread enters one side on the moving hearth and passes with the hearth through the heated chamber and when baked is removed from the opposite end. The hearth travels through the heated chamber at such a rate of speed that the bread is just baked during the time it passes through.

Draw Plate Oven. This type of oven contains a steel hearth on wheels which is loaded with bread when drawn out and then wheeled into a heated chamber or oven and drawn out when baked and removed.

Mixing Operations. *Revolving drum mixers* operate on the principle of mixing by compression and friction due to gravity. The materials are placed in a drum which contains horizontal rods passing through and when revolving the materials are lifted up and tumble over and through the rods until thoroughly mixed.

Kneading arm mixers are constructed on the principle of hand kneading and are composed of a bowl into which the materials are placed and a large steel arm running into the material in the bowl. The adhesion of the material to the arm causes a pull and stretch when the arm is withdrawn and a compression when the arm is run in, thus causing a thorough mixing.

Revolving arm mixers are constructed on the principle of steel arms revolving within the materials until thoroughly mixed. This type is largely used in America and are many in form, such as single-arm mixers, double-arm mixers with reversing principle, high- and low-speed, water-cooled and other details of construction. In recent years many forms, types and principles of dividing, molding, rounding up, and proofing machines have been invented and placed on the market, such as pocket dividers, belt molders, pocket and belt proofers.

The Science of Baking

The various chemical ingredients or compounds which enter into the process of bread baking are as follows: Protoplasm, enzymes, proteins, carbohydrates, acids, fats, esters, alcohols, oxides of carbon, mineral matter, water.

Protoplasm. Various forms of organisms exist in bread and the structure of these bacteria is chiefly protoplasm.

Enzymes are a class of chemical substances which cause most of the changes occurring during the production of bread. Thus it is understood that peptase has the property of splitting the higher proteins, as gluten of wheat, into the simple protein form such as albumins and amino bodies. The globulin (gluten) of wheat flour, which is insoluble in water, is digested and broken down into a soluble form during dough fermentation. This is accomplished by the activity of peptase in the dough, which is incorporated to a small extent with the flour itself, but more abundantly with the yeast. The peptase which exists in the interior of the yeast cell is

termed " endotryptase," and is excreted by the yeast in order to digest the insoluble protein (gliadin and glutenin) material surrounding the yeast cell to simple soluble forms so that they can be absorbed by the yeast as food. The result of the action of endotryptase of yeast and the peptase of flour is known to the baker as " ripening of the dough." The activity of the proteolytic enzymes (endotryptase and peptase) not alone modifies the gluten in the direction of greater elasticity (ripening of the dough) but producing from the peptonization of the globulin (gluten) certain simpler substances known to the chemist as the albumins and amino bodies. The latter nitrogenous substances are in the best form for yeast nourishment and, consequently, act to stimulate and activate the yeast by affording it increased nutriment, which increases the number of yeast cells and gas evolving power of each cell. The yeast in its enlivened condition also tends to separate into individual cells and thus disintegrate the cell aggregations so often formed by baker's yeast of to-day. These cell clusters produce irregularity of texture with oftentimes larger holes. The digestion of the gluten to albumins by the proteolytic enzymes referred to, aids in forming a flaky texture, since this class of substance coagulates with heat (becomes insoluble by the heat of the oven). Thus the peptic digestion is beneficial not alone in that it modifies that gluten in the direction of greater elasticity, but also produces the albumins, a class of proteins which are so changed by the heat of the oven to give a flaky texture, thereby causing a whiter appearance of the crumb (this action is similar to the change occurring during the boiling of the white of an egg). The invigoration of the yeast causes the production of a large number of fermentation gas cells, thereby producing a greater volume per weight of bread, and an even, uniform texture.

Proteins. The properties and the economic production of bread may be readily influenced by a group of chemical substances similar to the white of an egg and to gluten of wheat called *Proteins*. The group of proteins is composed of about five individual members, the properties of each varying somewhat from one another. The members of the protein family are the globulins, albumins, albumoses, peptones, and amino bodies.

Globulin. The best example of the first member (*globulin*) is gluten itself. The globulins are insoluble in water as gluten and meats. The importance of gluten in baking is well known. It is the material which forms the structure of a loaf of white bread, due to its elastic nature. The globulin (gluten) in a bread dough is broken down during fermentation into simpler proteins, even to such simple forms as the amino bodies which are used by the yeast as yeast food, and stimulate its multiplying power and vitality so that a much greater quantity of gas is evolved. Some commercial substances are sold on the open market, which contain besides other things, globulins which influence the properties of bread, resulting in a large loaf per weight of bread, with greater " life " in the dough stage, thus affecting the economic production of the bread. Gluten flours are

sold which contain a high per cent of globulins, and thus influence the digestibility and wholesomeness of the resulting bread.

Albumins. This family of nitrogenous substances belonging to the protein group is not as complex chemically as the globulins. The albumins are soluble in water and contain a property very valuable to the baker in that it coagulates with heat similar to the hardening of a white of an egg on boiling. The gluten is largely peptonized by the enzyme peptose to the albumin group, which dissolves into the free water of the dough. When placed in the oven, coagulation commences and flakes appear at the same time, producing a very white flaky crumb. The albumins are not used by the yeast as food, being much too complex in their nature to pass through the pores of the yeast cell membrane.

Commercial improvers are sold which contain albumins and which cause an improvement in the properties of bread and cause a white color of the crumb.

Albumose-peptones. Practically nothing is known concerning the sub-protein groups of albumoses and peptones, excepting that the peptones are partially used as yeast food.

Amino Bodies. This is the simplest group of proteins, being so simple that they readily pass through the yeast cell membrane and are readily metabolized into new protoplasm. This new protoplasm causes a reproduction of the yeast, resulting in a very large multiplication of the yeast. The increased nourishment afforded the yeast with its resultant invigoration produces increased yeast growth and a constant tendency to separate the yeast into individual cells and thus avoid cell aggregations. The individual cells will cause the production within a given time of a much larger amount of carbonic acid gas.

If the individual yeast cells comprising these clusters be undisturbed or insufficiently nourished, they remain intact, and through combined action of the aggregated cells cause the production of holes in the crumb, and a lack of uniformity in its texture. Due to the increased distribution of the invigorated yeast cells, combined with the larger number of the latter, each particle of dough becomes aerated and a greater volume of loaf results.

There are, at the present time, several so-called "flour improvers" sold on the market to bakers which contain amino bodies as an active principle. The properties of the bread are greatly improved in a number of particulars by the addition of these substances containing amino bodies to the bread dough. A greater volume per weight of bread results, with a fine texture due to the uniform distribution of the fermentation gas cells. The flavor is improved through a larger amount of alcohol-forming esters with the dough acids. The amino bodies also increase the digestibility and wholesomeness of the bread in providing an increase in nitrogenous substances easily absorbed by the human system.

Carbohydrates. One of the most complex carbohydrates is known

to the chemist as *cellulose*. This substance is totally insoluble in water, and its character can be changed only with difficulty. The substance known to the technical baker as crude fiber, contained in small amounts in flour, is composed chiefly of cellulose. So far as is known to-day, cellulose is objectionable in bread doughs. Flours containing large amounts of cellulose in the form of crude fiber are considered of less value for baking purposes than those flours which contain only small quantities, for crude fiber as contained in flour carries with it a brown color, which gives the resulting bread a darker crumb.

Cellulose, due to its extreme insolubility, under digestive conditions is considered by physicians as desirable in human food. The solid particles of cellulose, acting as roughage, thus aiding the elimination of waste products. Patents have been issued to an English inventor working in the field of bread-making, allowing him to add an enzyme cytase to bread doughs for the purpose of dissolving the cellulose present, thus making the bread much more readily digestible.

Starch. Starches can be obtained in three usual forms: Raw starch, gelatinized starch and soluble starch. Raw starch is that form of starch which exists naturally in nature, and forms the main portion of cereals. It exists in small, round, microscopical cells. The interior is termed starch granulose, and the exterior of the cell is termed starch cellulose. When this cell wall of starch cellulose is broken, the granulose is liberated and with water forms a jelly-like substance termed galatinized starch.

This same starch granulose, under certain conditions, will completely dissolve in water without forming a jelly-like substance, and in this condition is termed soluble starch. Raw starch has the property of absorbing a considerable quantity of water, and for this reason is beneficial in bread production when properly used, inasmuch as it effects the economic production of the bread. When raw starch in water is subjected to heat, the cells swell and finally burst, thereby forming gelatinized starch. Starch in this form and under favorable circumstances is readily changed by the enzyme diastase (existing in small amounts in flour and in large amounts in malt) to malt sugar and dextrin. However, at the temperature of dough fermentation 80° F., diastase is very nearly inactive. Therefore, very little change from starch to sugar occurs in the dough, even if the starch were in a gelatinized condition. If gelatinized starch is present in the dough, a slight inversion to sugar occurs during the time that the dough piece is in the oven, while baking, and then only during the time that the temperature remains within the limits of 100° F. to 170° F., because the activity of diastase is completely destroyed at a temperature above 170° F., and providing, of course, that diastase is present in the dough. Malt sugar and dextrin may be produced from starch by scalding raw starch, thus putting it in a gelatinized condition, and then adding some ground malt or high diastatic malt extract. The temperature at which this inversion of starch to sugar occurs must be between the limit of 100° F.

and 170° F. Sugar produced in this way and added to bread dough will result in a product of finer properties, especially in regard to color of the crust. Malt sugar, produced in this way from starches, does effect a noticeable improvement in the properties of the bread, and also diminishes the cost of bread production. Ordinary bakers' yeast is more accustomed to fermenting this sugar than cane sugar. This sugar is the same as that which yeast is allowed to ferment in its production within the walls of the factory, and yeast, like other living organisms, thrives best when under similar conditions throughout its life. When cane sugar is used for the production of gas, the yeast in the dough is under slightly different conditions to those to which it is accustomed, thus not giving the greatest rapidity of fermentation. Commercial materials may be purchased on the market, whose principal ingredient is starch in either a gelatinized or soluble condition, and which can be so used in a bread dough as to give exceedingly beneficial results, and, at the same time, economize the production of the loaf of bread.

Dextrins. Little is known concerning the influence of the dextrin in the production of bread. It is known, however, that dextrins exist in the dough and in the resulting bread, and that under certain conditions some of the starch in the dough is changed to dextrin and malt sugar. The influence of dextrin is undoubtedly most important in the chemistry of the crust of the bread. A large percentage of dextrins in a bread dough will cause a very hard crust on a loaf of bread. The class of substances known chemically as the dextrins become very hard and brittle when subjected to high moist heat.

Sugars. The influence of the group of chemical substances known to the chemist as the sugars is one of the most important. The character of the individual sugars plays a most important part in the proper fermentation of a bread dough. The influence of the sugars are known to the chemist, only a few concern the baker. The sugars which influence the properties of bread, and which should be understood most thoroughly (to produce a proper dough fermentation and to use proper baking conditions) are cane sugar, known as saccharose, malt sugar (maltose); corn sugar or glucose (dextrose), and milk sugar or lactose.

Saccharose. This is the chief constituent of commercial cane sugar, which is the sugar used to the greatest extent to-day by bakers throughout the world. Saccharose is very sweet to the taste, and sweeter than maltose, dextrose, or lactose; and, as a sweetening agent, saccharose is, therefore, the most effective. However, sugar in bread-making is used through yeast fermentation; and, in this capacity, saccharose is not the most desirable material. Mention has been made previously that yeast uses the sugars not as nourishment, but only as a means to secure energy to maintain its life functions. Under the conditions of manufacture the yeast is allowed to ferment, and develops in a media that does not contain saccharose, and, therefore, when this yeast is employed in a dough and used to create gas

from cane sugar, it must do so under different conditions from what it was previously accustomed to during its manufacture and development. It thus receives a shock, as it were, from which many minutes are required before it has recovered. Thus, a fairly long time is required for the " first rise " of the dough. Another property of saccharose that is exceedingly useful to the baker is that of caramelizing when subjected to high heat. Saccharose changes to caramel (a brown, sweet substance), when temperature conditions are favorable to this change. This property enables the baker by the addition of cane sugar to the dough to obtain a very deep brown color on the crust of the bread, which is deemed desirable by the majroity of the public in America. This color of crust is due to the caramelizaton of the sugar in the dough during the time of its baking in the oven.

Maltose. This sugar is very similar to saccharose in its chemical composition, but does not possess the sweet taste of the latter. This would be considered a desirable quality by many Americans whose palates tire of food products possessing even a slight sweet taste. Malt sugar (maltose) is the result of the inversion of starch by diastase, which process occurs commonly throughout nature. In all life processes, malt sugar is produced in this manner to be used by the living organisms as a source of life energy. Distillers' yeast, used by the baker to-day, is developed in a nourishing medium containing malt sugar (maltose) and has, in the course of its development, become accustomed to fermenting maltose into carbonic acid gas and alcohol to obtain energy to carry on its life functions. Maltose used in place of saccharose in a bread dough will improve the volume, texture, and color of a loaf of bread. Since the yeast cell is accustomed to fermenting maltose, its use in bread-making is desirable.

Fermentation is stimulated, and, consequently, an increased yeast-growth results. This greater stimulation tends to separate the yeast into individual cells, thus disintegrating the yeast cell clusters so often formed. The individual cells create each a fermentation gas cell in the dough piece during proofing, thus causing the bread to have greater volume and finer texture.

Maltose as saccharose caramelizes with high heat, but to a much greater extent and at a considerably lower temperature. Two doughs containing an equal amount of sugar at the time of baking (one, however, containing sugar in the form of maltose and the other saccharose) will result in two loaves of bread varying greatly in their depth of color. The one containing the maltose will have a much deeper color, since the color is due to the caramelization of the sugar. Malt sugar caramelizes at a fairly low heat The loaf of bread containing the maltose will also be less sweet to the taste, due to the greater sweetness of the saccharose. Commercial improvers which contain maltose can be purchased on the market. However, it is exceedingly difficult to obtain maltose as an article for sale, as it absorbs water rapidly, forming hard lumps.

Dextrose and Lactose. Dextrose is a less complex sugar chemically than either of the latter sugars. Both saccharose and maltose must first be changed to dextrose within the yeast cell before the enzyme zymase (existing also within the yeast cell) can ferment it to carbonic acid gas and alcohol. Bakers' yeast, however, can ferment dextrose directly to carbonic acid gas and alcohol. The use of dextrose, then, will allow a more rapid fermentation. Dextrose caramelizes at a very high temperature—higher even than saccharose; and for that reason less color is produced on the crust during baking when dextrose only is added to the dough. By using more than equivalent amounts of dextrose in the dough, the same depth of color will form on the crust of the bread as with the use of saccharose. Dextrose is the chief ingredient of sugars made by boiling starch with acid known as glucose, and sold by the bakers as an improver. Some other commercial improvers contain dextrose. Lactose is unfermentable by bakers' yeast.

Fats. The fat content of white flour varies from $\frac{1}{4}$ to $\frac{1}{2}$ per cent. Larger amounts of fats in flour are considered as dangerous to its keeping qualities. The baker adds from 1 to 5 lbs. of fat to the dough for each barrel of flour employed. The fat mellows the constituents of the dough producing a loaf soft to the palate and of more balanced food value. Liquid fats are preferred by bakers, due to the ease of handling, and also through the greater shortening effect of olein.

Esters. Flour is itself insipid to the taste. After fermentation its taste and flavor are modified and become very pleasant. This change is due to the formation during dough fermentation of a class of substances known as esters. They are formed by the combination of the alcohols in the dough (amyl, ethyl) with the dough acids as lactic acid and small amount of acetic acid. The characteristic aroma of baked bread is probably due to mellinoids.

Alcohols are formed during dough fermentation through the action of yeast on the various sugars of the dough. The enzyme zymase within the cell breaks down the sugar to alcohol and carbonic acid gas. While ethyl alcohol is produced in amounts equal to about one-half the weight of the sugar, amyl and butyl alcohol are formed in very small quantities.

Mineral Matter. The mineral matter in bread is received through the mineral content of the various materials employed. Water has been found to contain many minerals of value in baking and others which exert a harmful influence. Waters containing calcium sulphate and small amounts of magnesium sulphate stimulate the yeast during dough fermentation and cause a more rapid fermentation. Calcium carbonate in water has the reverse effect and is considered harmful. Ammonium chloride and calcium chloride added to bread dough in small amounts has been found to be beneficial.

Carbon dioxide is produced during dough fermentation by the action of yeast on the sugars of the dough. Carbon dioxide is formed equal to

nearly one-half the weight of the sugar fermented. The gas causes the material of the dough to expand and thus causes the dough to rise. The water of the dough absorbs the gas and becomes saturated. When the dough piece is placed in the oven the gas expands by the heat as the temperature rises. The gas-laden water of the dough no longer can hold the carbonic acid gas which comes out of solution causing the spring in the oven. The carbon dioxide of the dough remaining in the bread after baking gives the bread zest, especially when fresh.

Water. The water employed in baking bread effects the process of production by the ingredients which are dissolved in the water, such as proteins, sugar, etc. Water is one of the chief components of bread and forms about 40 per cent of its weight. It evaporates slowly and thus diminishes as the bread gets older and stale. About $\frac{1}{2}$ to 2 per cent of the water added to the dough evaporates during dough fermentation.

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